SYSTEMATIC ORGANIC CHEMISTRY

FOR

Higher Secondary and Intermediate Students of Indian Universities

by

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NEW
(FIFTH)
EDITION
Greatly Improved

1949

ATMA RAM & SONS
BOOKSELLERS, PUBLISHERS & STATIONERS
KASHMERE GATE, DELHI

Price Rs. 6/8/- only

Published by
RAM LAL PURY
of
Messrs. ATMA RAM & SONS
Kashmere Gate
Delhi

547
J 24 S 1/3 Cut
College.
Acc. No. 3998

First Edition, 1936
Second Edition, 1940
Third Edition, 1944
Fourth Edition, 1946
Fifth Edition, 1949

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Printed at
THE BHARAT MUDRAN
Delhi Gate
Delhi

PREFACE TO THE FIFTH EDITION

In preparing the manuscript for the fifth edition of *Systematic Organic Chemistry*, several alterations have been made to improve upon the earlier editions. The more important changes are :

(i) A section on Industrial Fractionation of alcohol (Chap. 2) has been added.

(ii) The sections on the Structure of the Atom and on the Electronic Theory of Valency (Chap. 6) have been entirely rewritten in the light of recent developments in this field.

(iii) A section on the Electrolytic Preparation of ethane (Chap. 7) has been added.

(iv) A section on nitrotoluenes (Chap. 29) has been added.

(v) Use of azo-dyes in Dyeing and Calico-printing has been explained more exhaustively (Chap. 31).

(vi) A reaction of phthalic acid with phenols involved in the production of *flouresceins* has been added (Chap. 35)

In preparing the *Index* an entirely new scheme, devised by my son, Chanan Singh Sekhon, a B.Sc. student, has been used. The folio headings have been altered accordingly.

All the blocks for the present edition have been made afresh and in some cases the figures have been redrawn to make them more explanatory. About fifty new blocks and a number of university questions have been added.

It is earnestly hoped that the book in the present form would be more useful to the student than its earlier editions.

Sikh National College,
Qadian.
November, 1949.

JAGINDAR SINGH

CONTENTS

CHAPTER.		PAGE.
	PART I—GENERAL	
1.	Introduction	1
2.	Methods of Purification and Criteria of Purity ..	5
3.	Qualitative Elementary Analysis	19
4.	Quantitative Elementary Analysis ..	23
5.	Determination of Empirical and Molecular Formulæ ..	30
6.	Molecular Structure and Isomerism	38
	PART II—ALIPHATIC OR OPEN-CHAIN COMPOUNDS	
7.	Saturated Hydrocarbons or Paraffins	48
8.	Unsaturated Hydrocarbons	64
9.	Halogen Derivatives of Hydrocarbons	79
10.	Monohydric Alcohols	91
11.	Ethers	108
12.	Aldehydes and Ketones	113
13.	Monocarboxylic Acids	134
14.	Acid Chlorides, Anhydrides, Amides and Nitriles ..	148
15.	Esters	156
16.	Fats, Oils and Soaps	162
17.	Amines and Nitro Paraffins	166
18.	Substituted Monocarboxylic Acids	175
19.	Polyhydric Alcohols	182
20.	Polybasic Acids	188
21.	Optical Activity and Stereoisomerism	200
22.	Carbohydrates	207
23.	Derivatives of Carbonic Acid	223
	PART III—AROMATIC COMPOUNDS	
24.	The Coal-Tar Industry	228
25.	Benzene	232
26.	Isomerism and Orientation of Benzene Derivatives and Orientating Influence of Substituents	236
27.	Homologues of Benzene	239
28.	Aromatic Halogen Compounds	243
29.	Aromatic Nitro Compounds	249
30.	Aromatic Amino Compounds	256
31.	Diazonium Salts	265
32.	Aromatic Sulphonic Acids	271
33.	Phenols	274
34.	Aromatic Alcohols, Aldehydes and Ketones	279
35.	Aromatic Acids	285
36.	Oxidizing, Reducing and Catalytic Agents used in Organic Chemistry	295
Appendix		300
I.	Atomic Numbers and Atomic Weights of some Elements ..	301
II.	Tension of Water Vapour in Millimetres of Mercury ..	301
III.	Useful Memoranda	302
Index ..	.. ..	308
Tables of Logarithms ..	.. .. ..	310
Tables of Antilogarithms	.. .. ..	

SYSTEMATIC
ORGANIC CHEMISTRY

PART I

GENERAL

CHAPTER 1

INTRODUCTION

1. Scope of Organic Chemistry.—Formerly, the name 'Organic Chemistry' implied the chemistry of substances obtained directly or indirectly from plants or animals. These substances were regarded as being capable of production only under the influence of the mysterious **vital force** or *life force*, and, hence, it was thought impossible that the chemist could produce any "organic" substance in the laboratory. It was believed that the living world laid aside the ordinary laws which controlled the formation of *inorganic* substances (*i e.* substances of mineral origin), and that it possessed its own laws of combination and its own force of affinity.

In 1814, Berzelius, by means of his improved methods of analysis, made accurate determinations of the composition of a number of organic acids. The results obtained proved clearly that the composition of each of these compounds could be represented by simple atomic ratio of the constituent elements. Thus, one of the distinctions between 'organic' and 'inorganic' substances disappeared.

The chief distinction that was supposed to exit between organic and inorganic substances, *viz.*, that the former were produced only by the agency of life force, was given a rude shaking by the work of Wohler, a famous German chemist, who, in 1828, succeeded in preparing urea from ammonium cyanate. The preparation of alcohol from ethylene by Hennel in the same year and a host of other syntheses effected subsequently gave a death-blow to the '**Vital Force Theory**'.

The time-honoured terms 'organic' and 'inorganic' are still retained by the chemist, though the significance attaching to them at present is entirely different from what it was originally. To-day the name **Organic chemistry signifies the chemistry of carbon compounds,** as the element carbon has been found to be the invariable constituent of all substances of vegetable and animal origin. We do not, however, draw the line between two branches of chemistry too sharply, for such substances as carbon monoxide, carbon dioxide, carbon disulphide, carbonates and cyanides, which being carbon compounds, should be included in text-books of organic chemistry, are, in actual practice, discussed in text-books of inorganic chemistry.

2. Chief Reasons for Distinction between Organic and Inorganic Chemistry.—If the same fundamental laws apply to organic and inorganic chemistry, as they certainly do, and if the distinction between

the two branches is not a sharp one, why should the two be treated separately? We give below the chief reasons for keeping up the distinction :—

(1) The atoms of carbon possess a remarkable capacity for combining with one another, giving rise to "chains" and "rings". Compounds are known in which as many as sixty carbon atoms are directly linked to each other, while others contain "closed chains" or "rings" composed of as many as thirty carbon atoms. It is because of this

FRIEDRICH WOHLER
(1800-1882)

Well-known German chemist, whose discovery of the *synthesis of urea* from ammonium cyanate dealt a death-blow to the "Vital Force Theory" of the formation of organic substances.

remarkable property of carbon that the number of organic compounds is practically unlimited. Thus, the number of organic substances already known is about ten times as much as that of the compounds not containing carbon, the former being more than a quarter of a million and the latter about 26,000.

(2) The second point which distinguishes organic from inorganic chemistry is the phenomenon of "Isomerism," which is of so common occurrence in organic chemistry. Thus whereas the formula H_2SO_4 represents only one substance, namely sulphuric acid, the formula C_2H_6O stands for *two* different substances—ethyl alcohol and dimethyl ether. Compounds related to each other in this manner are called isomers and the phenomenon is called isomerism. There are numerous other cases of isomeric substances of which we shall here cite only—camphor which has as many as 119 known isomers.

(3) In the third place, the reactions of organic chemistry differ in certain important points from inorganic reactions. The majority of the latter are ionic in nature, and take place almost instantaneously, while the former proceed comparatively slowly. Moreover, the reactions of organic chemistry are much more complex, and the same substances, when allowed to react together under different conditions, may give rise to different products. Thus, ethyl alcohol, when treated with sulphuric acid, may, according to experimental conditions produce four different substances, namely ethylene, ethyl ether, ethyl hydrogen sulphate and diethyl sulphate.

(4) Lastly, organic compounds differ in many ways from inorganic compounds. They are unstable and are generally decomposed at high temperatures. They are usually soluble in alcohol, ether, benzene, etc., whereas majority of the inorganic conopunds are insoluble in these solvents; but they dissolve in water. Again, organic compounds are much more complex, *e.g.*, *stearin*, a constituent of animal fats, is represented by the formula $C_{57}H_{110}O_6$. Substances such as cellulose, starch, and proteins are even more complex.

From the considerations outlined above it is clear that the separate treatment of organic from inorganic chemistry is based on the principle of division of labour and convenience of the workers in the two fields rather than on any fundamental difference between the two branches.

3. Importance of Organic Chemistry.—Numerous organic substances play an important part in our daily life. The clothes we wear, the food we eat, the wood we employ for making the furniture for our homes, the paper and ink we use in writing, the soap we employ for washing, dyes and drugs that are so indispensable to us, are all organic in nature. The study of organic chemistry is necessary to the student of Biology for the proper understanding of the various processes taking place in the bodies of animals and plants, to the physician, in order to know the nature of disease and its cure, the pharmacist, for the proper preparation of medicines, and above all to the chemical manufacturer. Of the numerous industries based on organic chemistry we may mention manufacture of alcohol and wines, petroleum industry, textile industry, rayon manufacture, manufacture of paper, leather industry, manufacture of dyestuffs, and manufacture of drugs.

4. Sources of Organic Substances.—The different sources from which various organic substances are derived are given in the following table:—

Source	*Substances*
1. Plants	Sugar, starches, cellulose, alkaloids, acids, esters, vegetable oils, essential oils, camphor, gums, dyes, perfumes, tannins, etc.
2. Animals	Fats proteins, urea, uric acid, gelatin, etc.
3. Coal-tar	Benzene, toluene, phenols, and other aromatic compounds.
4. Wood	Methyl alcohol, acetone, and acetic acid.
5. Bones	Pyridine, quinoline, etc.
6. Petroleum	Petrol, solvent naphtha, kerosene, gas oil, lubricating oils, vaseline, paraffin wax, etc.

5. Elements present in Organic Compounds.—Though there exist numerous compounds of carbon, most of them contain this element in combination with one or more of the elements hydrogen, oxygen and nitrogen; a few of them contain chlorine, bromine, iodine, sulphur, phosphorus or arsenic. The following table gives the composition of the more important classes of organic compounds :—

Elements Present	*Classes of Compounds*
C and H	Hydrocarbons.
C, H and O	Alcohols, aldehydes, ketones, carboxylic acids, esters, oils, fats, sugars, starch, cellulose, etc.
C, H and N	Amines.
C, H, N and O	Amides, amino-acids, nitro-compounds, proteins, alkaloids.

QUESTIONS

1. What is meant by the Vital Force Theory ? Why was it abandoned ? How does the modern chemist define 'Organic Chemistry' ?

2. What considerations have led the chemist to separate the Organic Chemistry from Inorganic Chemistry ?

3. Write a short essay on "The Importance of Organic Chemistry."

4. What are the main sources from which various organic substances are obtained ? Name the various elements which are met with in most organic substances.

CHAPTER 2

METHODS OF PURIFICATION AND CRITERIA OF PURITY

1. Purif cation of Organic Substances.—Most of the organic substances when first prepared are impure. Before they can be systematically investigated it is necessary that they should be obtained in a pure state. The various methods employed for this purpose are given below.

2. Crystallization.—The method of purifying an organic substance by crystallization is essentially the same as that employed for inorganic compounds, except that solvents such as alcohol, ether, light petroleum, chloroform, benzene etc., are employed in addition to water. A hot, nearly saturated solution of the substance in a suitable solvent is first prepared. Any insoluble matter that may be present is filtered off, and the clear, hot solution allowed to cool; crystals of the substances separate out, while the impurities are left behind in the mother liquor. The details of the procedure are :—

(1) ***Preparing the Solution.*** The first thing to do in this connection is the selection of the right solvent. Small amounts (a few milligrams will suffice) of the substance are put into a number of small test tubes, and treated with a small quantity of each of the common solvents. If the substance dissolves immediately in the cold, or if practically no dissolution occurs on warming, the solvent under trial is unsuitable. The most suitable solvent will be that in which the substance dissolves on heating and from which it readily crystallizes out on cooling.

Having made a selection of the solvent, we must next determine the amount of it to be used. It should be just sufficient to make the solution, when hot, nearly saturated. Too large an excess of the solvent should be avoided, otherwise no crystals will form on cooling. It should be remembered that the substance to be purified often contains insoluble impurities, and no attempt must be made to bring these into solution by the addition of a large amount of the solvent.

A suitable quantity of the well powdered substance along with the necessary amount of the solvent, is placed in a flask. If solution occurs readily, the flask is gently warmed on a water bath. Should it, however, be too slow, the flask is fitted with a reflux condenser and heated on the water— or sandbath (Fig. 1). This arrangement prevents the loss of the solvent by evaporation during the process of solution, and also prevents the vapour of the solvent, if inflammable, from catching fire.

(2) ***Filtering the Hot Solution.*** If the quantity of the solution is small, it may be filtered through an ordinary filter paper placed in a glass funnel with a short stem or a fluted filter, fitted into a fluted funnel. In either case, the funnel and the filter paper must be warmed just before filtering.

In case the amount of the solution is large, the glass funnel containing the filter paper is placed in a **hot water funnel** (Fig. 2). This consists of a double walled copper funnel provided with a side-tube, *S*, for heating. It must be remembered in this connection that if the vapour of the solvent is inflammable, the flame *must* be put out before starting the actual filtration.

(3) ***Crystallizing***. The hot filtrate is allowed to cool as slowly a possible in a beaker covered with a watch-glass. In this manner, large beautiful crystals are obtained. For analytical work however small-sized, pure crystals are required These are readily obtained by cooling the solution rapidly, say by placing the beaker in cold water. The crystals thus obtained are free from droplets of the mother liquor, which the large crystals are very liable to occlude.

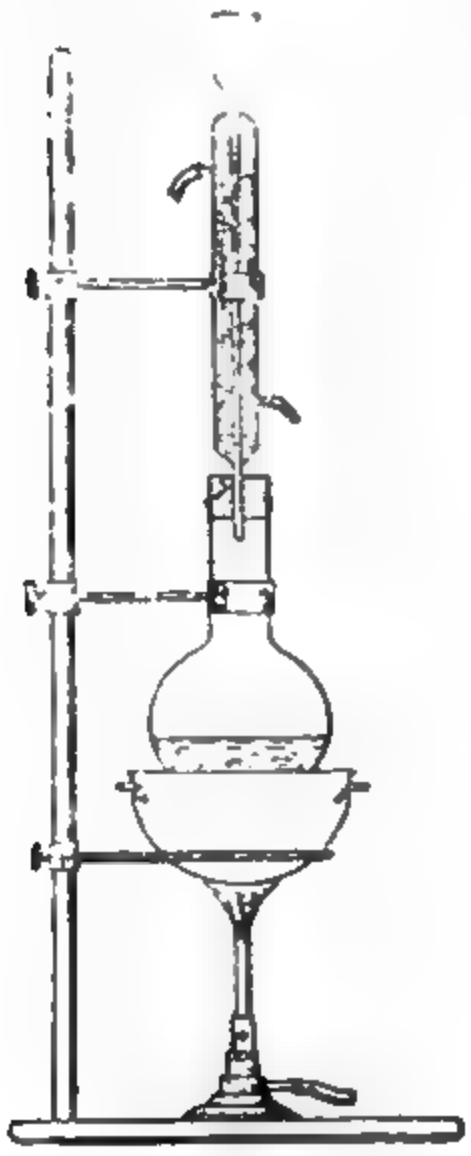


Fig 1

In the case of certain substances, on allowing the hot solution to cool, an oily liquid may separate out instead of the crystals. This indicates that the solution is too much concentrated, and the solute therefore, begins to separate at a temperature above its melting point. The defect may be remedied by adding a little more of the solvent.

(4) ***Separating the Crystals from the Mother Liquor*** If the crystals are large the mother liquor can be readily poured off and the crystals washed with a little of the pure solvent. The best method however, of separating the crystals from the mother liquor is that of "vacuum filtration", using a **Buchner funnel**, *B*, a filtering flask, *F*, and a **filter pump**, *P* (Fig. 3). The trap, *T*, prevents the liquid left in the body of the pump from being sucked into the filtering flask.

For handling larger amounts of material in technical operations, a **centrifugal machine** is most frequently used.

Fig. 4. shows a centrifugal machine for drying crystals, designed by Professor Richards of Harvard University. It is specially suitable for chemical and sugar laboratories The crystals to be dried are put into the perforated drum, *D*, made in this case of porcelain. The outer bucket, *B*, is also of porcelain and is provided with a draining nozzle, *N*. The drum is made to rotate at a speed of 1,000 revolutions per minute, by means of the electric motor, *M*. The dry crystals are left inside the drum, while the mother-liquor, which previously adhered to the crystals, passes out through the perforations into the outer bucket.

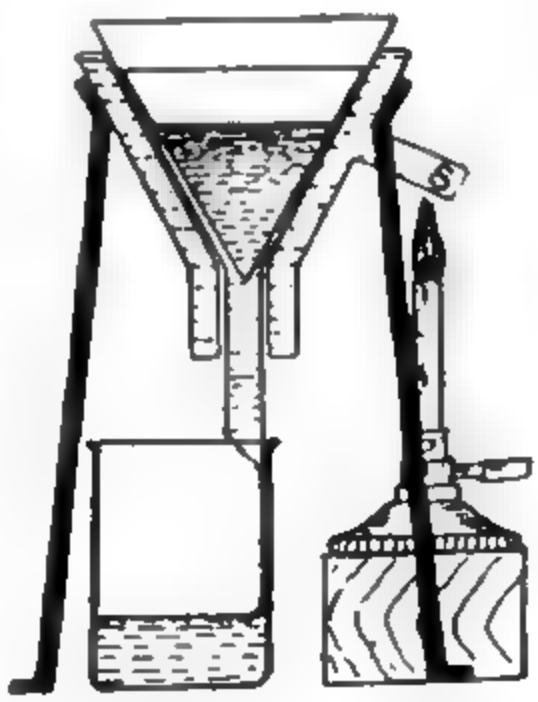


Fig. 2. Hot water Funnel

Expt. 1. Dissolve an impure sample of acetanilide in hot water. Add a little animal charcoal and filter the hot liquid using a hot water funnel Allow the filtrate to cool. Acetanilide separates out in shining, colourless plates. Separate the crystals, using a Buchner funnel and a suction pump (Fig 3), and wash them with a little water.

3. Sublimation.—A simple method of sublimation consists in placing the substance to be sublimed on a watch-glass heated very slowly on a sand-bath with a free flame. The watch-glass is covered with an inverted funnel, somewhat smaller than itself (Fig. 5). Over the edge of the funnel is stretched a perforated filter paper. This prevents the very small, light crystals of the substance from falling back on to the

watch glass. The upper surface of the funnel may be kept cool by covering it with several layers of wet filter paper.

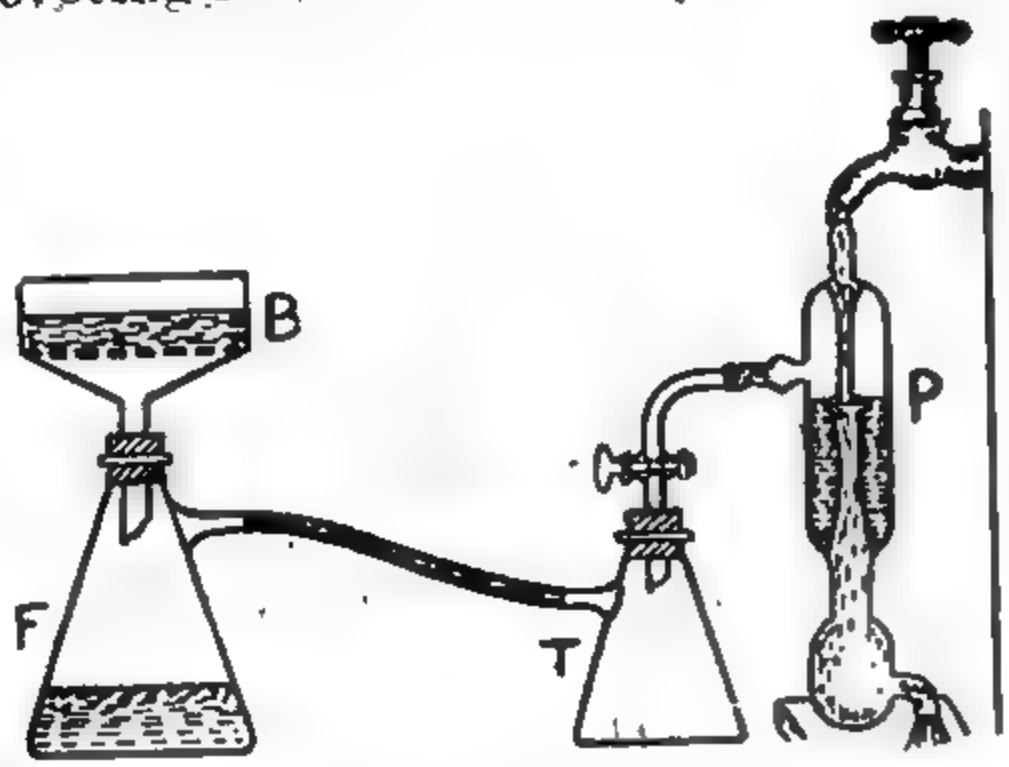


Fig. 3. Filtration under Reduced Pressure. (*B*) Buchner Funnel. (*F*) Filtering Flask. (*T*) Trap. (*P*) Suction Pump.

A very efficient apparatus for sublimation is Bruhl's apparatus shown in Fig. 6. This consists of a hollow metal vessel provided with inlet and outlet tubes for circulating water, and having in the middle an opening of the shape of an inverted, truncated cone. The substance to be sublimed is placed in a crucible supported in the opening as shown in the figure, and the whole is covered with a glass dish. The substance sublimes in part on the inside of the glass dish, but more abundantly on the upper cold surface of the metallic vessel.

Expt. 2. Using the apparatus shown in Fig. 5 or Fig. 6, prepare a sample of pure benzoic acid or anthracene.

4. Distillation.—The process of distillation is used for freeing a substance from non-volatile impurities, or from substances which are far more or far less readily volatile than the substance to be purified.

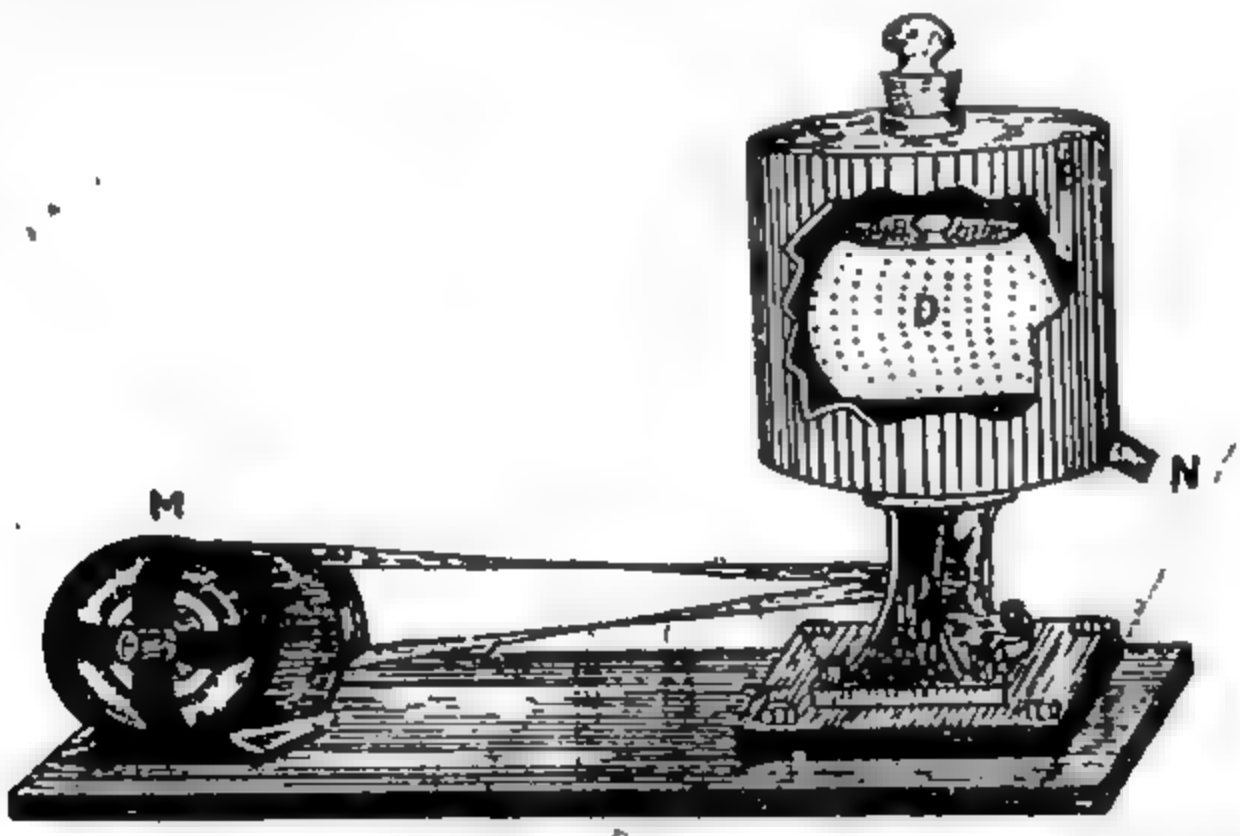


Fig 4. Centrifugal Machine worked by an Electric Motor.

The usual form of apparatus employed in distillation is shown in Fig. 7. It consists of :—

(1) *Distillation flask*, *F*, provided with a side-tube,
(2) *Liebig condenser*, *C*, and
(3) *Receiver*, *R*.

A thermometer, *T*, is usually fitted into the neck of the flask, in order to note the boiling-point of the liquid. The bulb of the thermometer must be just below the position where the side-tube is fused into the neck of the flask. The end of the side-tube of the distillation flask must pass right through the cork, so that the distillate, as it falls into

the condenser tube, does not come into contact with the cork. To prevent the liquid from "bumping" (sudden, violent ebullition), a few pieces of broken porous tile (or some glass beads) are added to the liquid before starting the distillation

Fig. 5. A simple Apparatus for Sublimation.

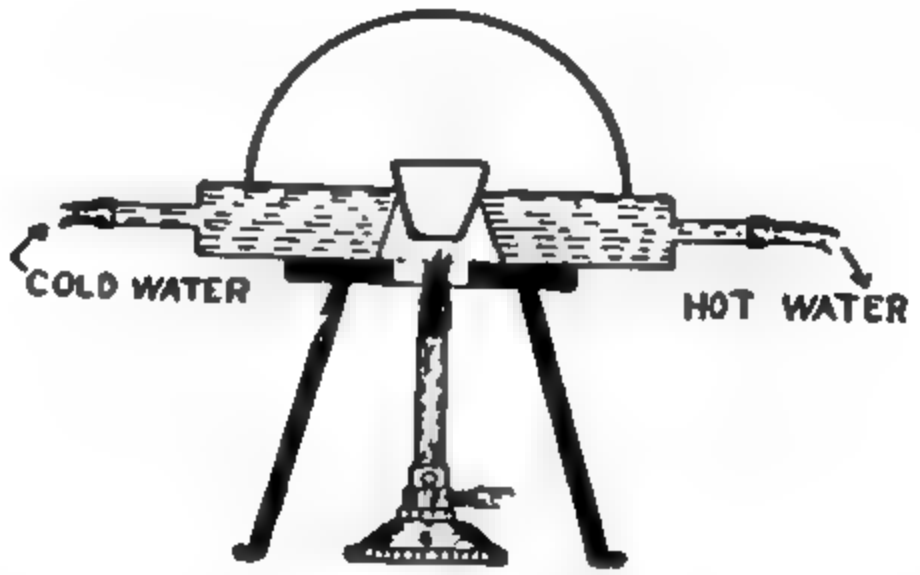


Fig. 6. Bruhl's Sublimation Apparatus.

When the boiling-point of the liquid lies above 170° C, there is a great danger of the condenser tube getting cracked. In such a case, therefore, a straight glass tube, called an air condenser (Fig. 8) is used instead of the water cooled condenser.

Expt. 3. Using the apparatus given in Fig. 7, distil some pure benzene. Add a few pieces of porous tile to prevent bumping. Notice that practically the *whole* of benzene passes over at a constant temperature (*i.e.* 80° to 80·5° depending upon the atmospheric pressure).

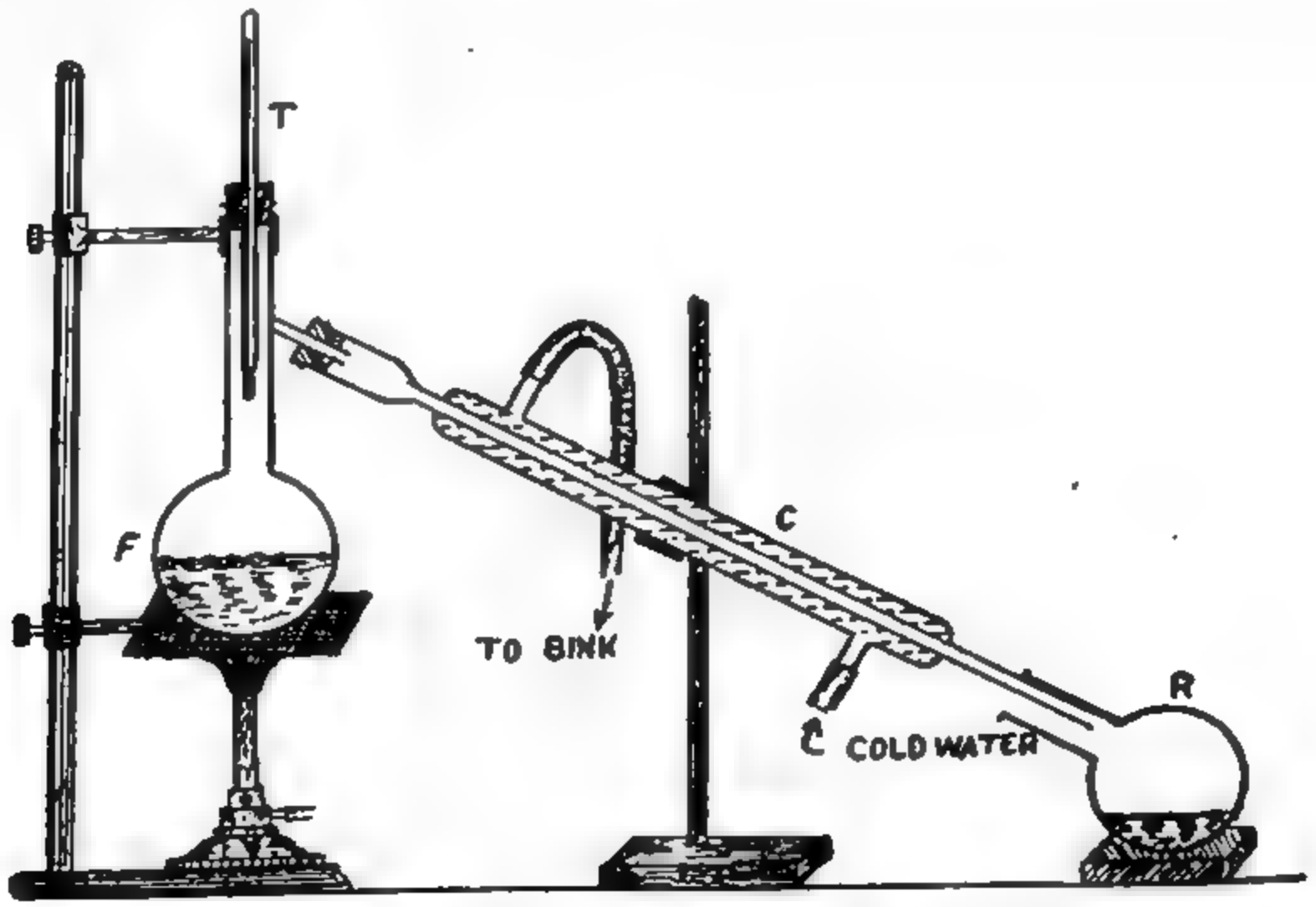


Fig. 7. Distillation and Boiling-point Apparatus.

Expt. 4. Using an air-condenser distil some aniline, which has turned dark in colour. Notice that the first few drops are turbid, because of the presence of

moisture. As soon as the distillate passes clear, receive the aniline (b.p. 183°) into a clean, dry flask.

5. Fractional Distillation.—This process is employed for separating a mixture of two or more miscible liquids, the boiling-points of which are sufficiently removed from one another. The method is similar to ordinary distillation, except that portions of the distillate passing at different temperatures are collected separately. The boiling must be made to proceed slowly and evenly, so that it may be possible to count the individual drops as they fall into the receiver.

On distilling a mixture of two liquids, say, benzene (b.p. 80°) and toluene (b.p. 111°), more of the lower boiling liquid passes over at the beginning, and more of the higher boiling one at the end of the operation, the composition of the distillate changing continuously. In order to effect a separation of benzene toluene mixture, the distillate may be best collected in 5 fractions: *A*, from 80° to 85°; *B*, from 85° to 91°; *C*, from 91° to 98°; *D*, from 98° to 105°; *E*, from 105° to 111°. The different fractions are collected in labelled flasks, and their respective volumes noted. The portion of the liquid which does not distil upto 111° is rejected.

Fig. 8. Air Condenser.

The process of distillation is now repeated as follows: The contents of flask *A* are transferred to the distillation flask, and redistilled, the distillate passing at 80—85° being collected in the same flask *A*. When the temperature reaches 85° the distillation is stopped, and the contents of the flask *B* added to the distilling flask. The distillation is continued once again, and the fraction passing at 80—85° is collected in flask *A*, and the one passing at 85°—91° in flask *B*. As soon as the temperature reaches 91° the distillation is again stopped, and the contents of flask C, allied. The distillation is once more continued and the fractions passing at 80°—85°, 85°—91° and 91°—98° are collected in flasks *A*, *B*, and *C*, respectively. The process is carried on in the above manner, until all the fractions have been added.

The five fractions collected during the second distillation are submitted to the same process as before, and the operation repeated, the volumes of the fractions *A* and *E* increase, while those of fractions *B*, *C*, and *D* continuously decrease. When the total amount of the liquid in flasks *B*, *C*, and *D* becomes very small (say less than one-tenth of the total amount of the liquid) the refractionation may be stopped.

The process of fractional distillation may be carried out in a **fractionating flask**, *i.e.*, a distillation flask with a sufficiently long neck. The process, however, is rendered more efficient and rapid by using a **fractionating column** (Fig. 9), connected to the neck of the boiling flask. The fractionating column aids the separation by working in the opposite way to the boiling process. As the vapour passes upward through the column, it gets partially condensed by the cooling action of the air. The condensate flows down the column and forms a layer around each disc, glass-bead or ring contained in the column,

In this manner, the up-going vapour is brought into a continuous contact with the down flowing liquid, whereby the vapour is thoroughly scrubbed. The scrubbing aids the separation both by partial evaporation of the liquid, and by partial condensation of the vapour. There occurs, therefore, a continuous exchange of constituents between the vapour and the liquid. Thus, by the time vapour reaches the top of the column, most of the less volatile constituent would get condensed. Similarly, the more volatile constituent contained in the down-flowing liquid would be completely removed by the time the latter flows back into the distilling flask. In this manner, a far more thorough separation of the constituents is effected than is possible with an ordinary long-necked distillation flask. The use of a fractionating column renders the number of redistillations much smaller, though as a rule, it cannot entirely do away with the necessity of redistilling.

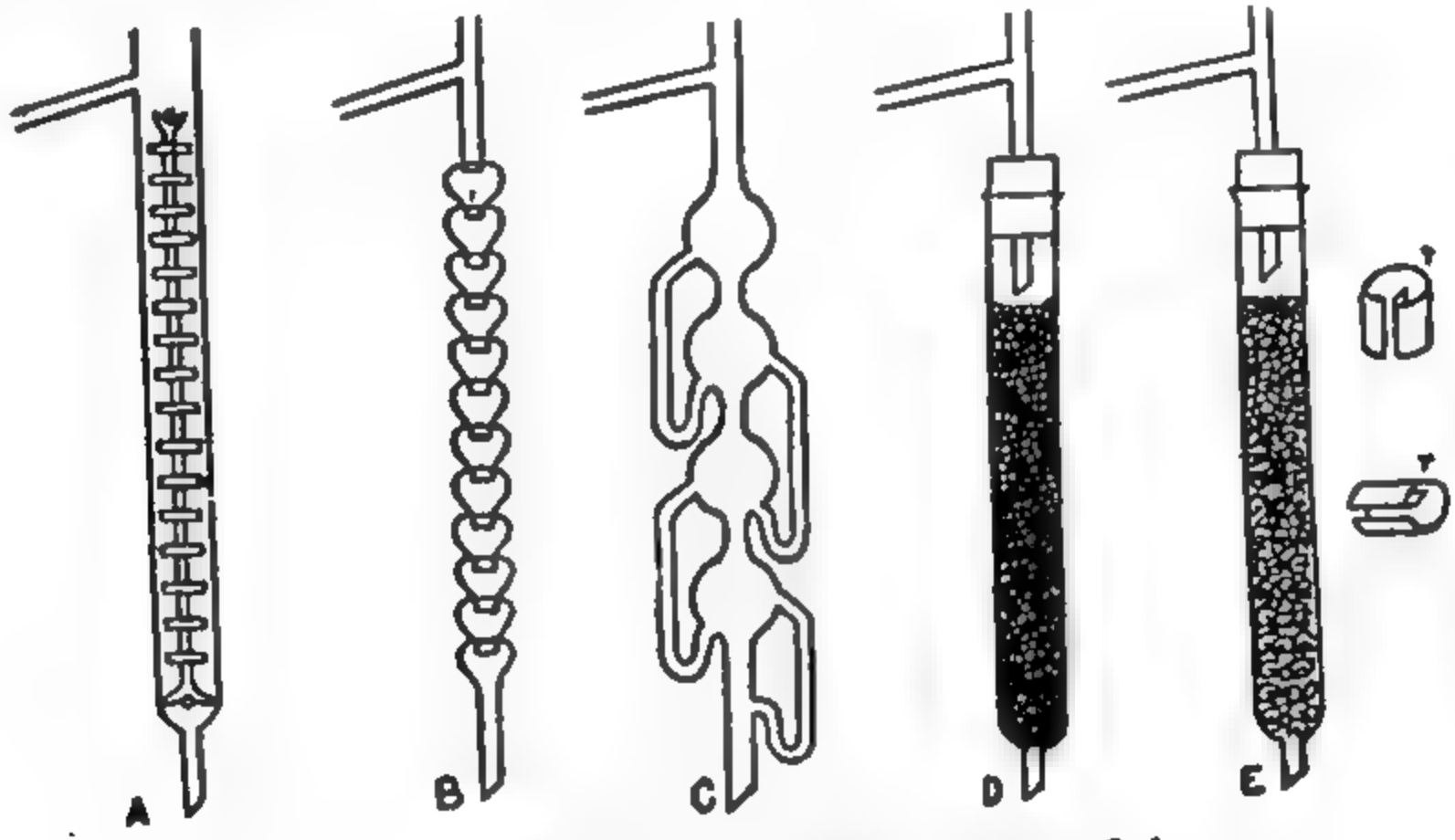


Fig. 9. Different Types of Fractionating Columns.

(*A*) Young's rod-and-disc type ; (*B*) Young's pear-shaped type : (*C*) Le Bel-Henninger column ; (*D*) Hempel's column filled with glass beads ; (*E*) Still head filled with Lessing's contact rings R,R (shown on a large scale on the right of *E*).

The apparatus used in fractional distillation on the laboratory scale is shown in Fig. 10. The mixture is distilled from a round-bottom flask, *F*, fitted with a fractionating column, *FC*. The latter is provided with a thermometer, *T*, and is connected to a water-cooled condenser, *C*. The successive fractions of the distillate are collected in the receivers R_1, R_2, R_3, and R_4.

6. Industrial Fractionation.—For the separation of mixtures of volatile liquids on a commercial scale very carefully designed fractionating columns are used which may attain a height of 30 feet or more. The Coffey still used for rectifying aqueous alcohol, the long air-cooled vertical columns employed for the separation of the crude petroleum into various fractions, and the plants employed for the fractionation of 90 per cent and 50 per cent benzol, to obtain pure benzene, toluene and xylene, are important examples of the use of fractionating columns in chemical industries.

Fig. 11 shows the bell-and-plate fractionating column frequently used in industrial fractionation. The mixed vapour from the still, *S*, enter

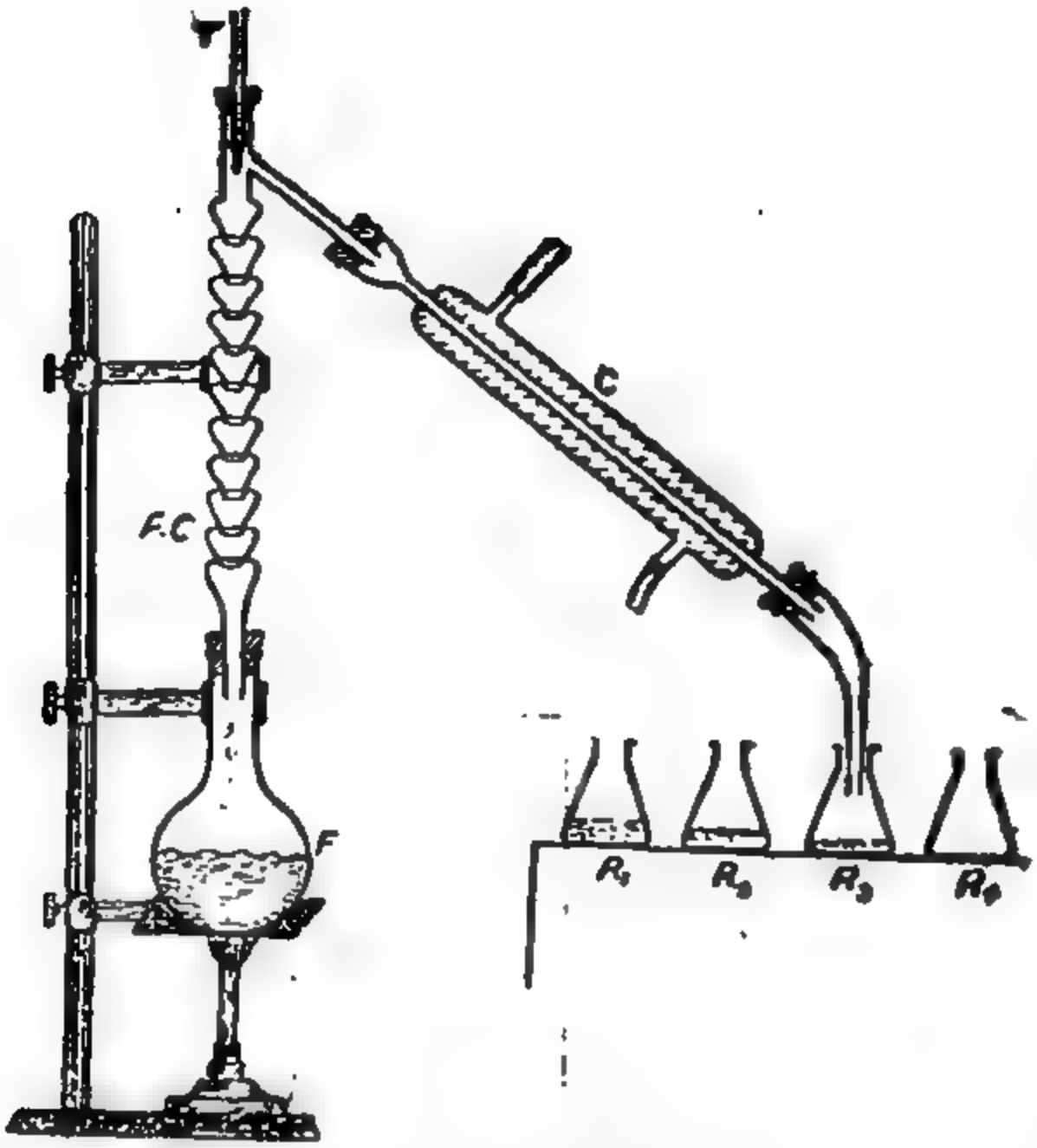


Fig. 10. Fractional Distillation.

compartment 1 of the fractionating column, as shown by arrows in the figure. Here they get partially condensed, and the condensate, consisting of the higher boiling constituents, collects on the plate. An overflow pipe allows the condensate to flow back into the still. The more volatile components pass on to compartment 2, and so on. In this manner, the lower-boiling components get separated from the higher oiling bones. The former may be led off from the top of the column and the latter withdrawn from the bottom.

Expt. 5. Using long fractionating column packed with Lessing's contact rings made of aluminium, or with small pieces of glass tubing, distil a 1:1 mixture of benzene and toluene. Collect 5 fractions and measure their respective volumes. Repeat the fractionation a second time and again measure the volumes of different fractions.

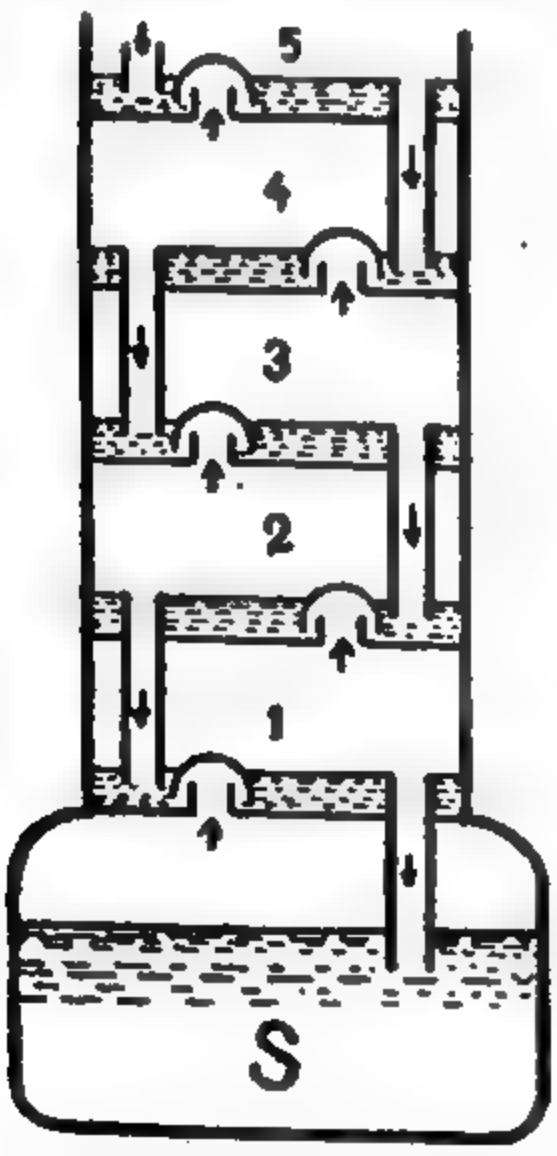


Fig. 11. Bell and plate Fractionating Column.

7. Distillation under Reduced Pressure.—Some organic liquids which decompose at their boiling point under atmospheric pressure may be distilled without decomposition under low pressure. Thus glycerine boils with partial decomposition at 290° under 160 mm. pressure. It may be distilled without decomposition at 180° under a pressure of 12 mm.

The usual form of apparatus used in "**vacuum distillation**" is shown in Fig. 12. The liquid to be distilled is placed in a Claisen's distilling flask, *F*. Through one of the necks of the flask passes a thermometer *T*, and through the other a glass tube, *C*, which is drawn out at its lower end to a capillary dipping into the liquid and is closed by means of a piece of rubber tubing and a screw clamp. This arrangement prevents bumping, which is more pronounced during vacuum distillation than during distillation under ordinary pressure. The evacuation of the apparatus is effected by means of a water or mercury pump. In the former case, the lowest pressure obtainable is that of aqueous vapour at the room temperature (*i.e.*, usually 10 to 25 mm). With a mercury pump, pressures lower than 1 mm. can be readily obtained. A manometer, *M* is introduced between the receiver and the pump to

ascertain the pressure under which the distillation takes place. All corks must be made perfectly air-tight by coating them with collodion after the apparatus has been fitted up.

In most of the distillations under reduced pressure it is necessary to collect the distillate in fractions. Many ingenious forms of receiver have been devised, so as to allow the collection of various fractions without breaking the vacuum. The best known of these arrangements is the **triangle apparatus** shown in Fig. 12. When it is desired to change the receiver, the cock *J* is turned off, *K* is turned on, while the three-way cock *L*, is turned so that the receiver is put in communication with the outside air and not with the pump; meanwhile the distillate goes on

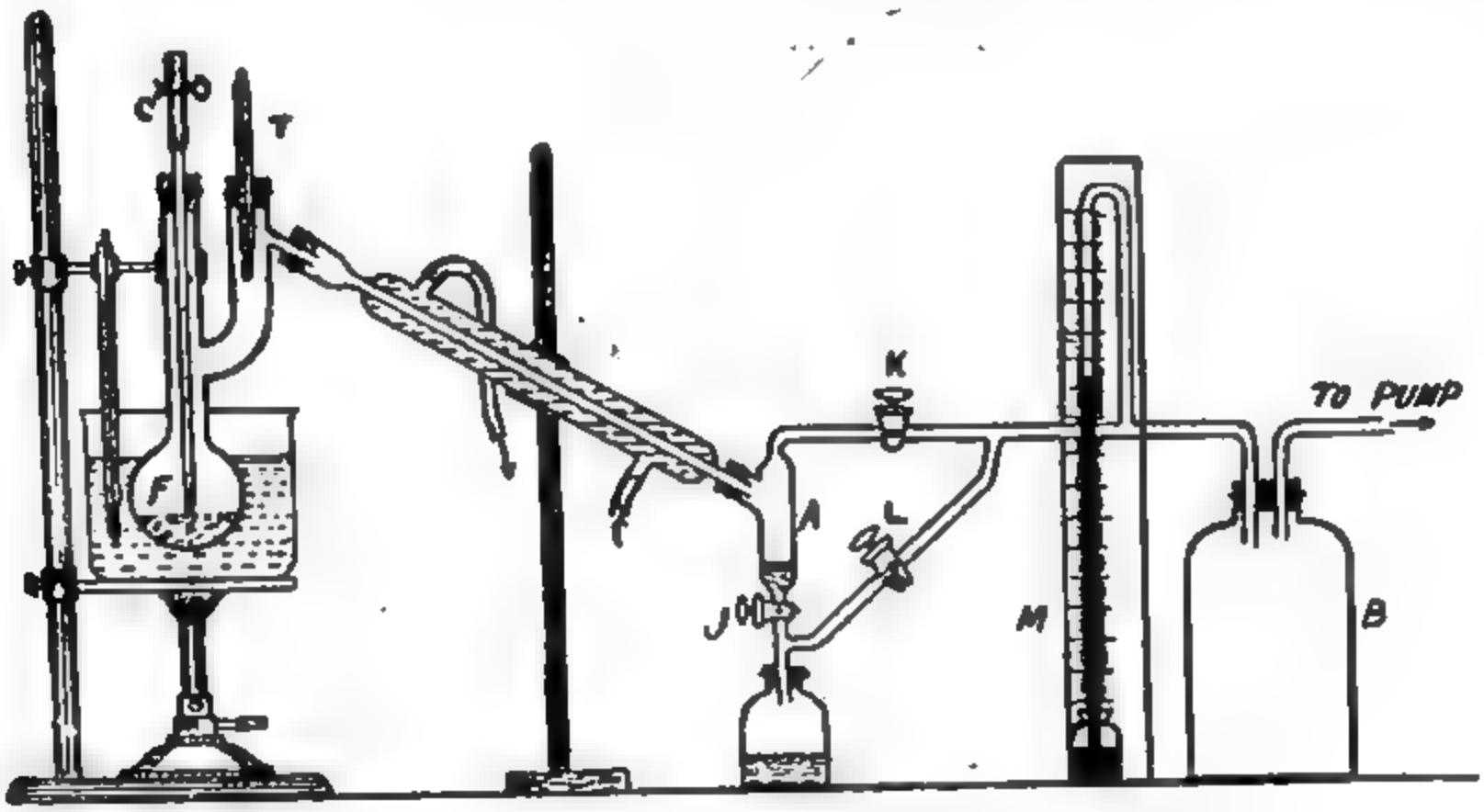


Fig. 12. Distillation under Reduced Pressure.

collecting in *A*. The receiver is now changed, the cock *L* is turned so that the receiver is once again put into communication with the pump. After a short time, the cock *K* is closed and *J* opened, so that the distillate in *A* flows down into the new receiver.

8. Steam Distillation.—The process of steam distillation is employed for separating those substances which are appreciably volatile at 100° from non-volatile components of a mixture. The apparatus employed is shown in Fig. 13. The mixture to be treated, along with some water, is placed in a large-size, round-bottom flask, *F*, heated on a sand-bath and connected to a condenser, *C*. The flask is held in a sloping position so that during the vigorous ebullition, which occurs, none of the mixture may be thrown up into the tube leading to condenser. Steam from the boiler *B* (which generally consists of a tin can provided with a safety tube, *S*) is rapidly passed through the liquid in the flask *F*. The heating of *P* and *F* is controlled, so as to keep the quantity of the liquid in *F* constant. In the case of an oily liquid or a solid substance, the distillation should be continued for about 15 minutes after drops of oil, or particles of solid, have ceased to appear in the condenser. In the case of a soluble acid, the distillation should be stopped when the distillate no longer gives an acid reaction with litmus.

The distillate in the receiver consists of water and the substance whose separation is desired. In case the substance is an oily liquid, it is separated from the water by means of a **separating funnel (Fig. 14)**;

if it is an insoluble solid, it is separated by filtration. If the substance is a soluble acid, the liquid is exactly neutralized with sodium carbonate, and the solution evaporated to dryness. From the pure salt, thus obtained, the acid may be recovered by distilling with sulphuric acid. The substances that are usually purified and separated by the process of steam-distillation are : aniline, bromobenzene, *p*-dibromobenzene, essential oils, petroleum, turpentine oil, etc.

Expt. 6. Fit up the apparatus shown in Fig. 13. Place some well powdered *ajwain* made into a thin paste with water into the flask, *F*. Carry on the steam-distillation of the substance, until no more oily drops of *ajwain oil* pass over. Separate the oil by means of a separating funnel

Fig. 13. Apparatus for Steam Distillation

Expt. 7. Carry ont the steam-distillation of the oleo-of-turpentine (*ganda barora*). The distillate consists of *turpentine oil* and water; the residue consists of *rosin*.

9. Principle of Steam Distillation.—In the process of steam distillation two volatile substances take part :(*i*) water, and (*ii*) the substance whose separation is desired. In case the two substances are mutually immiscible, the vapour pressure of each is unaffected by the presence of the other. When the mixture is boiling, the sum of the vapour pressures p_1 and p_2 of the constituents must equal the atmospheric pressure, P. That is,

$$P = p_1 + p_2.$$

The boiling point of the mixture must, therefore, be even lower than that of the lower boiling constituent at the atmospheric pressure Hence, in steam-distillation the same object is achieved as in distillation under reduced pressure, *i.e.*, the boiling of a substance is effected at a temperature lower than its actual boiling point at the atmospheric pressure.

10. Extraction with Solvents.—The process of extraction with solvents is employed in the following three cases :—

(1) ***Isolation of a Substance Dissolved or Suspended in a Liquid*** (usually Water). The separation of the substance is effected by agitating the liquid with a solvent in which the substance is more readily soluble but which is not miscible with the first liquid, drawing off the solution of the substance in the new solvent, and distilling off the latter. The most commonly used solvent for this purpose is ether, though in certain cases carbon disulphide, petroleum ether, chloroform, and benzene are also used.

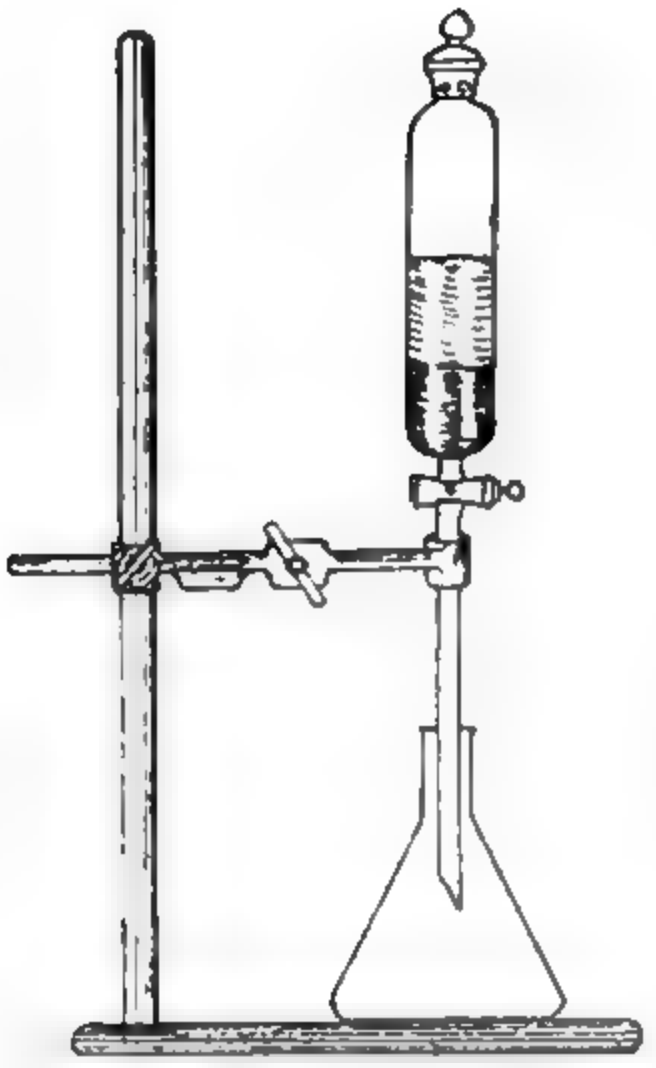


Fig. 14 Separating Funnel.

A familiar example of ether extraction is that of aniline. This substance is prepared by the reduction of nitrobenzene, and is separated from the reaction mixture by steam-distillation. The distillate separates into two layers; a lower layer of aniline and an upper layer consisting of an aqueous solution of aniline, which also contains a quantity of aniline in the form of minute droplets that do not settle quickly (*i.e.* an emulsion). The lower layer can be separated by means of a separating funnel, and presents no difficulty. To recover aniline from the aqueous layer, it is shaken up with ether, in which solvent aniline is much more soluble than in water, and the upper ethereal solution of aniline is separated from the lower aqueous layer by means of a separating funnel. The lower aqueous layer is once again shaken with a little more of ether, and the ethereal layer again separated. Finally, aniline is recovered by boiling off the ether.

(2) ***Isolation of a Substance from a Solid Material.*** The more important examples of extraction of this type are: the extraction of alkaloids from leaves and bark of plants, of flavouring extracts from seeds, and of oils from crushed seeds and oil cake.

The **Soxhlet Extractor** (Fig. 15), which is frequently used in chemical laboratories for the extraction and estimation of fat or oil in a material (*e.g.*, oil seeds and oil cake), is a very convenient apparatus for this purpose. The powdered material is put into a *thimble*, *T*, made of stout filter paper, and placed inside the glass tube, *G*. The latter is provided with a syphon, *S*, and a side tube, *S.T.* The length of the thimble should be such that it extends about 1 cm. above the highest point of the syphon tube. The amount of solvent taken in the boiling flask *F* should be 1½ to 2 times the volume of *G* up to the highest point of the syphon. The flask, *F*, is heated on a water or sand-bath, according to the nature of the solvent. The vapour of the solvent rises through the side-tube up into the water-cooled condenser, *C*. The condensate drops into the thimble, dissolves the substance and filters out into the space between the thimble and the glass tube. As soon as the liquid level in *G* reaches the highest point of the syphon, the solution automatically flows back into the boiling flask. The process may be continued for as long a time as necessary. At the end of the operation, the solvent is boiled off and the isolated substance weighed, if necessary.

Expt. 8. Arrange the Soxhlet extractor on a water bath. Introduce a weighed quantity of crushed cocoanut into a thimble or a filter paper cylinder. Use petrol as the extracting solvent. The upper end of the condenser should preferably be provided with a long piece of rubber tubing to carry off the unconden ed inflammable vapour of petrol to a hood or waste-sink. At the end of the operation, evaporate off the petrol, and weigh the residual cocoanut oil.

(1) ***Removal of Soluble Impurities from Mixtures.*** This is of great importance in the purification of organic substances. The principle

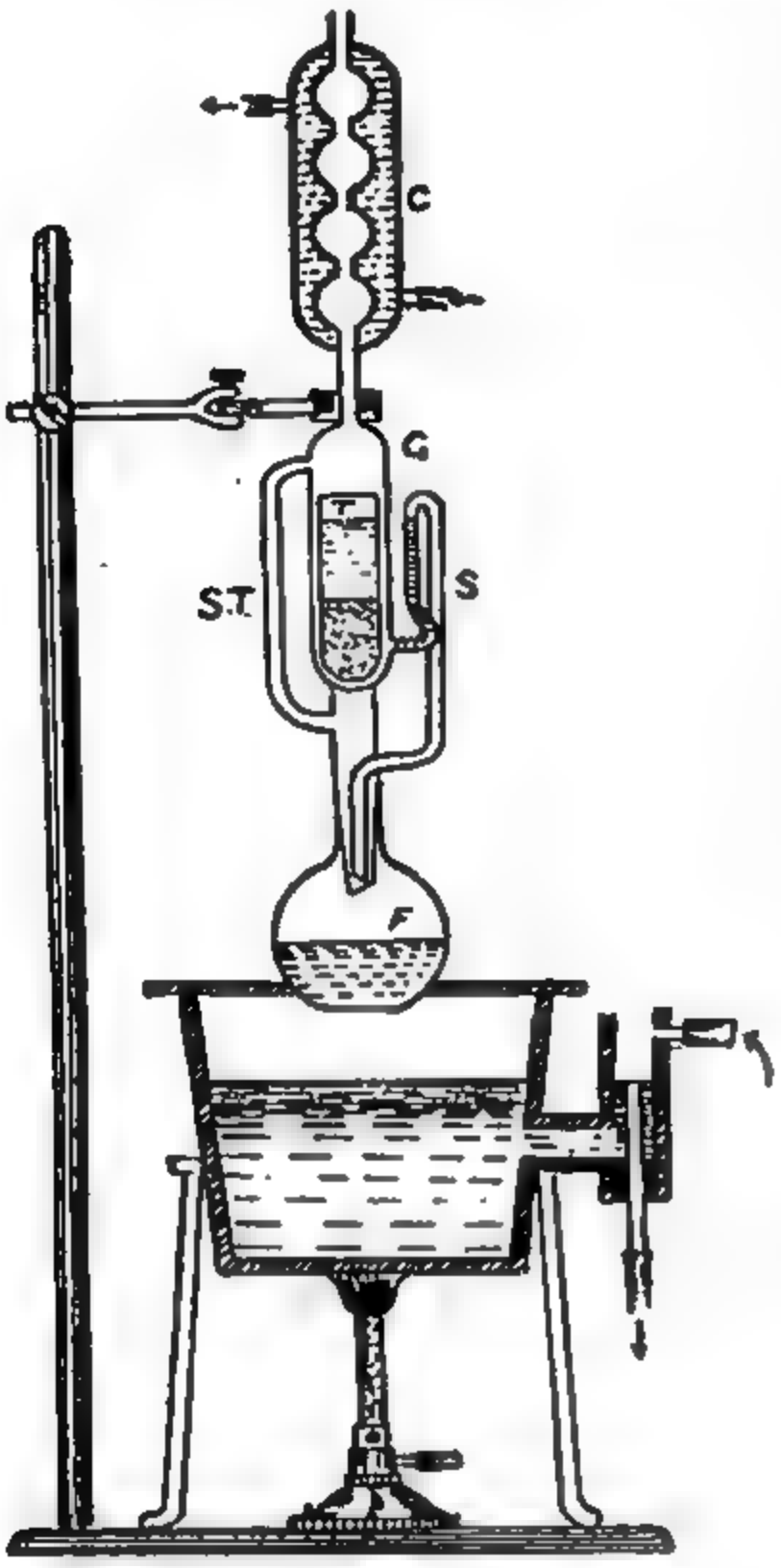


Fig. 15. Soxh et Extractor.

involved is similar to (2) except that the solvent extracts the impurities, leaving behind the desired substance in a more or less pure condition. Here as in (2), several extractions with small portions are more effective than a single extraction with the whole of the given quantity of the solvent.

11. Treatment with Animal Charcoal.—Animal charcoal finds considerable application in organic chemistry to free a colourless substance from coloured impurities, and also impurities of a tarry character. The substance in the liquid state, or in solution in a suitable solvent, is boiled with the requisite quantity of animal charcoal and filtered. If the solvent used (or the substance itself, if liquid) be immiscible with water the animal charcoal, which is generally moist, is dried on a water bath before use.

Expt. 9. Boil a solution of brown sugar in water (or a weak solution of magenta) with animal charcoal in a dish, and filter. Notice that the filtrate is colourless.

12. Drying of Organic Substances.—No organic substance can be regarded as pure if it contains even traces of moisture. The drying of starting materials and of finished preparations is, therefore, an important part of organic practical work.

Solid substances are dried in a number of ways. If sufficiently stable, they may be dried in a steam— or air-oven, or by heating on a free flame. If unstable on heating, the substance is allowed to stand in the air, or, better still, in a vacuum desiccator (Fig. 16) containing a suitable drying agent.

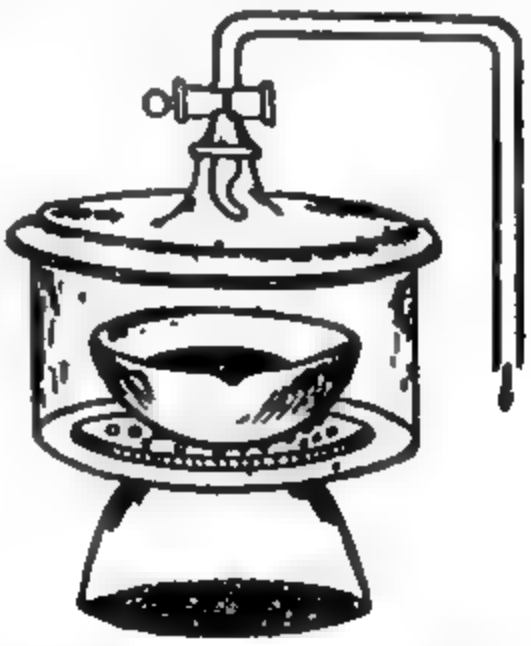


Fig. 16. Vacuum Desiccator.

Before a solid substance is finally dried, as given above, the adhering moisture must be removed (1) by pressing it between folds of filter paper, (2) by pressing it on an unglazed procelain plate, or (3) by means of a centrifuge (Fig. 4).

Organic liquids, or solutions of organic solids and liquids in suitable solvents are dried by letting the liquid stand in contact with a suitable drying agent. The drying agent employed in a particular case must satisfy the following conditions :—

(1) It must be practically insoluble in, and chemically indifferent towards, the liquid to be dried :

(2) It must remove water efficiently.

A list of suitable desiccating agents for different classes of organic

substances is given below :—

Substance	Desiccating Agents
1. Hydrocarbons and Ethers.	Anhydrous calcium chloride, metallic sodium, phosphorus pentoxide.
2. Alcohols.	Quicklime, anhydrous potassium carbonate, anhydrous magnesium or sodium sulphate.
3. Haloid Derivatives.	Anhydrous calcium chloride, anhydrous magnesium sulphate or sodium sulphate.
4. Aldehydes and Ketones.	Anhydrous magnesium sulphate or sodium sulphate, anhydrous calcium chloride
5. Organic Acids.	Anhydrous magnesium sulphate or sodium sulphate, phosphorus pentoxide
6. Organic Bases.	Solid potassium hydroxide, quicklime or soda-lime.

As a rule, *the spent drying agent is separated before distilling off the dried liquid.* If this point is not attended to, the hydrate of the salt produced during desiccation may be dissociated on heating and, hence, the liquid passing over remains moist. In the case of metallic sodium, phosphorus pentoxide and quicklime the removal of the desiccating agent before distillation of the liquid is unnecessary, as the drying agent undergoes a chemical reaction with water to produce a stable, non-volatile product.

A very easy and efficient method of drying organic liquids and solutions of organic substances in suitable solvents is based on the principle of steam-distillation. Thus, when moist aniline is distilled (Expt. 4), at first a few drops of a turbid liquid, consisting of a mixture of aniline and water, pass over; then follows a clear distillate consisting of pure dry aniline. Again, when a solution of a moist organic substance in benzene is distilled, the first few drops consist of a mixture of benzene and water, the mixture distilling at a temperature lower than the boiling point of pure benzene (80° C). After this, the benzene itself passes off, and the dry organic substance is left as a residue.

13. Methods of Testing the Purity of a Substance. The following are the common methods for testing the purity of an organic substance:—

(1) **Melting point.** The usual method for testing the purity of a solid organic substance is the determination of its melting point. This may be done in two different ways :—

(i) If a comparatively large amount of the substance is available, about 20 grams of it are carefully heated in a wide test-tube, provided with a thermometer, and a ring stirrer. When about three-quarters of the substance has melted, the burner is put out, and the liquid well stirred. The thermometer is read every half minute. The temperature at which the mercury column remains stationary for 2 to 3 minutes is taken as the melting point of the substance.

Since the melting point is defined as the temperature at which the liquid and the solid form of a substance can exist side by side, it is absolutely necessary that at the time of reading the thermometer *both the solid and the liquefied substances are present, and that the temperature remains constant for a pretty long period.* If the whole of the substance happens to melt, some more of the solid substance must be stirred in, and the lowest constant temperature reached should be noted.

Expt. 10. Using the apparatus described above determine the melting point of naphthalene or ortho-nitrophenol.

(ii) In most cases, however, the quantity of the substance available for the melting-point determination is small. For this reason, the usual method employed in chemical laboratories is as follows : A small quantity of the substance is finely powdered and introduced into a capillary tube, closed at one end. The capillary containing the substance is then moistened with concentrated sulphuric acid, and placed alongside a thermometer, suspended in a beaker containing concentrated sulphuric acid, in such a way that (*a*) the substance in it is at the same level as the middle of the bulb of the thermometer, and (*b*) a little more than half of the capillary stands above the surface of the liquid (Fig. 17). This latter arrangement makes the tube cling to the thermometer by capillary attraction.

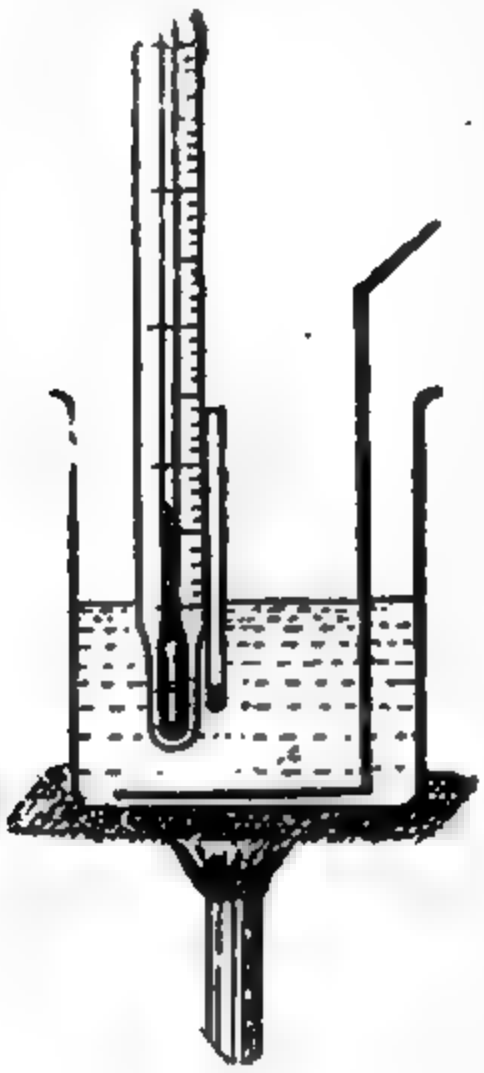


Fig. 17.
Determination of Melting point.

The acid in the beaker is now heated with a small flame, and constantly stirred with a curved stirrer made of thin glass rod, the substance and the thermometer being closely watched all the time. The *moment* the substance melts and becomes transparent, the temperature indicated on the thermometer is recorded. The experiment should be repeated, using a *fresh* tube and fresh substance.

A pure solid has a perfectly definite and sharp melting point. Hence :

(*i*) If the given compound does not melt sharply, it should be taken as impure.

(*ii*) If the identity of the given compound is known, its melting point is determined experimentally and compared with the true melting point, as given in tables of physical constants. If the two values agree, the given compound may be taken as pure. If however, the melting point of the compound is found to be lower, it is evidently impure

(*iii*) If the identity of the compound is not known, the melting point of the specimen is first determined. It is then recrystallized from a suitable solvent, and the melting point determined once again. If there occurs no change in the melting point, the compound may be taken as pure. But if the second melting point be higher than the first the compound is impure.

Expt. 11. Using concentrated sulphuric acid or glycerine bath, determine the melting point of urea (132°), iodoform (119°) or meta-dinitro benzene (90°). Should the sulphuric acid of the bath turn dark during the experiment, it can be rendered colourless by adding a drop of concentrated nitric acid or a crystal of sodium nitrate.

(2) **Boiling Point.** In order to decide whether a given liquid is pure or impure, its boiling point is determined by distilling it from a small distillation flask provided with a thermometer (Fig. 7, *p*. 9). If the liquid is pure, the whole of it would distil at a constant temperature. If, on the other hand, the boiling point rises during distillation, the liquid is impure.

For a correct boiling-point determination, the following points must be carefully attended to :—

(*i*) The bulb of the thermometer should be *wholly* surrounded by

most conclusive test for nitrogen. A freshly cut, small piece of sodium is melted in a hard-glass test-tube; a small amount of the substance is then added on to the molten metal, and the mixture is gradually raised to a red heat. Under these conditions, the nitrogen and the carbon of the compound combine with sodium to form sodium cyanide:

$$Na + C + N \rightarrow NaCN$$

The tube, while still hot, is plunged in to some distilled water in an evaporating basin. The liquid is boiled, filtered, and tested for cyanide radical as follows:—

Its reaction towards litmus paper is first noted, which should be *alkaline*, owing to the formation of sodium hydroxide by the action of water on the excess of sodium. The alkaline solution is warmed with a few drops of ferrous sulphate and a little ferric chloride, and rendered acidic with concentrated hydrochloric acid. The formation of a blue precipitate, or a green coloration, proves the presence of a cyanide in the solution, and, therefore, of nitrogen in the given organic compound.

The explanation in the above test for cyanide is that ferrous hydroxide, produced by the action of sodium hydroxide on the ferrous salt, reacts with the cyanide to produce sodium ferrocyanide.

$$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4$$
$$Fe(OH)_2 + 6NaCN \rightarrow 2NaOH + Na_4[Fe(CN)_6],$$

which with the ferric salt, gives a precipitate of Prussian blue when the solution is acidified:

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

Expt. 2. *Lassaigne's Test.* Take a bright piece of sodium in a 3-inch test-tube of hard glass and add a *small* quantity of urea. Heat the tube gradually, and finally raise the temperature to bright redness. Break the hot tube in about 10 c.c of distilled water contained in a dish. Stir up the liquid with a glass rod and filter. To the filtrate add a few drops of ferrous sulphate solution and a drop or two of ferric chloride. If the liquid be alkaline, a green precipitate of ferrous hydroxide will be produced at this stage. If no precipitate is formed, make the liquid alkaline with sodium hydroxide solution. Heat to boiling and then acidify with hydrochloric acid. Formation of a blue precipitate or a green coloration proves the presence of nitrogen in the substance.

(2) **Soda-lime Test.** In a comparatively small number of nitrogenous substances, the presence of nitrogen can be detected by heating the substance with soda-lime. If ammonia is evolved, the presence of nitrogen in the substance is proved. Should, however, the test be negative, it does *not* prove the absence of nitrogen. Nitro-compounds, for instance, do not respond to this test.

Expt 3. *Soda-lime Test.* Heat some urea with soda-lime in the test-tube. Test the evolved gas for ammonia with litmus or turmeric paper. Show that no ammonia is evolved when dinitrobenzene is heated with soda-lime.

5 Detection of Sulphur.—(1) **Lassaigne's Test.** This is applied in exactly the same manner as for nitrogen. The sulphur is converted into sodium sulphide, which is detected as given in Expt. 4.

Expt. 4. Fuse thio-urea or sulphanilic acid with metallic sodium as in Expt. 2. Extract the fused mass with water, and filter. Test the filtrate as follows: (*i*) To a few drops add a freshly prepared solution of sodium nitro-prusside; transient, beautiful violet coloration. (*ii*) Place a drop of it on a silver coin; black stain of Ag_2S. (*iii*) Acidify a few drops with acetic acid, and add lead acetate; a heavy black ppt. or a dark coloration.

(2) *Oxidation to Sulphuric Acid.* Readily volatile substances usually do not respond to Lassaigne's Test. They are heated at 200° to 300°C

with fuming nitric acid in a "bomb tube" (see Sec. 6, Chap. 4). Under these conditions, sulphur gets oxidized to sulphuric acid, the formation of which is detected by the barium chloride test.

6. Detection of Halogens.—(1) **Beilstein's Test.** By this test the presence of a halogen in an organic substance can be detected very quickly and conveniently. A piece of copper wire is heated in the oxidizing flame until it ceases to impart a green colour to flame. It is then taken out of the flame, and a minute particle of the substance containing halogen is placed on it. The heating in the flame is repeated. At first a luminous flame may be produced, owing to the burning of carbon. This is soon followed by a green, or bluish green, coloration, owing to the vaporization of the cupric halide.

Beilstein's test, though very simple and delicate, cannot be applied in the presence of acids and traces of metallic halides. It is also given by certain compounds containing no halogen, *e.g.*, urea, volatile cupric cyanide being produced in this particular case. Further, the test does not differentiate the halogens. In case of doubt, or when it is desired to identify the halogen present, apply the following test.

Expt. 5. *Beilstein's Test.* Show by means of this test that cane sugar contains no halogen. Further, show that the test is positive when urea (a compound containing *no halogen*) is employed.

(2) **Lassaigne's Test.** In this test substance is heated with sodium as in the detection of nitrogen. The fused mass is extracted with water and the solution filtered. The filtrate is strongly acidified with nitric acid and boiled so as to decompose the cyanide or sulphide, if present. Silver nitrate is the reagent; a precipitate of silver chloride (white), bromide (pale yellow) or iodide (yellow) shows the presence of chlorine, bromine or iodine in the substance under examination.

The necessity of boiling the filtrate with nitric acid arises out of the fact that if the substance contains nitrogen or sulphur, sodium cyanide or sulphide is formed. The former gives with silver nitrate a *white* and the latter a *black* precipitate.

Expt. 6. *Lassaigne's test.* Using Lassaigne's test show that chloroaniline (or quinine hydrochloride) contains a halogen. Note that the precipitate formed with silver nitrate is turned violet on exposure to light, and is readily soluble in cold dilute ammonia. Hence, the halogen present is chlorine.

7. Detection of Phosphorus.—The presence of phosphorus in an organic substance can be determined by heating it with (*a*) fuming nitric acid under pressure, (*b*) sodium peroxide, or (*c*) a mixture of sodium carbonate, and nitrate. The phosphorus is thus oxidized to phosphoric acid or sodium phosphate, which is tested with ammonium molybdate in the usual manner.

8. Detection of Metals.—To identify the metal present in an organic substance the latter is ignited on a piece of platinum foil. The residue is then examined for the common metallic radicals by the usual methods of inorganic analysis.

QUESTIONS

1. How would you know whether a given compound is organic or inorganic ? *(Punjab, Inter., 1925)*

2. How can you prove that ethyl alcohol is a compound of carbon, hydrogen and oxygen ? *(Uned Prov. Inter., 1921)*

given an organic compound, describe how you would proceed to detect the presence of C, H, N, and Cl. Explain as far as possible, the reactions involved in the process. (*Benares, Inter., 1926.*)

6. Describe in detail, giving formulae and equations, how to detect nitrogen in a compound (*United Prov. Inter., 1935*)

1. The quantitative estimation of various elements in an organic substance is known as **quantitative elementary analysis.** The following methods are in use for the estimation of elements.

2. Estimation of Carbon and Hydrogen.—Liebig's Method. These two elements are always estimated in one operation, known as **"combustion".** A weighed amount (about 0·2 gm.) of the substance is heated with cupric oxide in a stream of oxygen, free from carbon dioxide and water vapour. The carbon contained in the substance is thereby burnt to carbon dioxide, and the hydrogen to water. The gaseous products of combustion are passed through (i) a U-tube filled with anhydrous calcium chloride which absorbs water vapour, and (ii) potash bulbs containing a strong solution of caustic potash, which absorbs carbon dioxide. The increase in weight of (*i*) multiplied[1] by $\frac{2}{18}$ gives the amount of hydrogen and the increase in weight of (*ii*) multiplied[1] by $\frac{12}{44}$ gives the amount of carbon in the substance analysed.

The complete set-up of the apparatus for the estimation of carbon and hydrogen is shown in Fig. 1. The various parts of the apparatus from left to right are :—

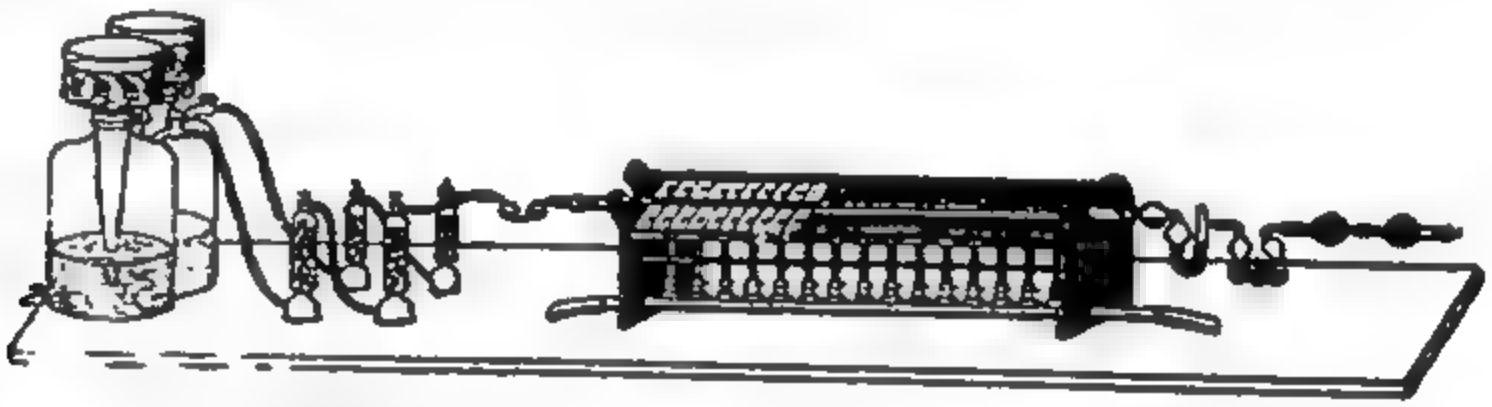


Fig. 1. Complete Apparatus for the Estimation of Carbon and Hydrogen.

(1) Two glass reservoirs, one containing oxygen and the other air.

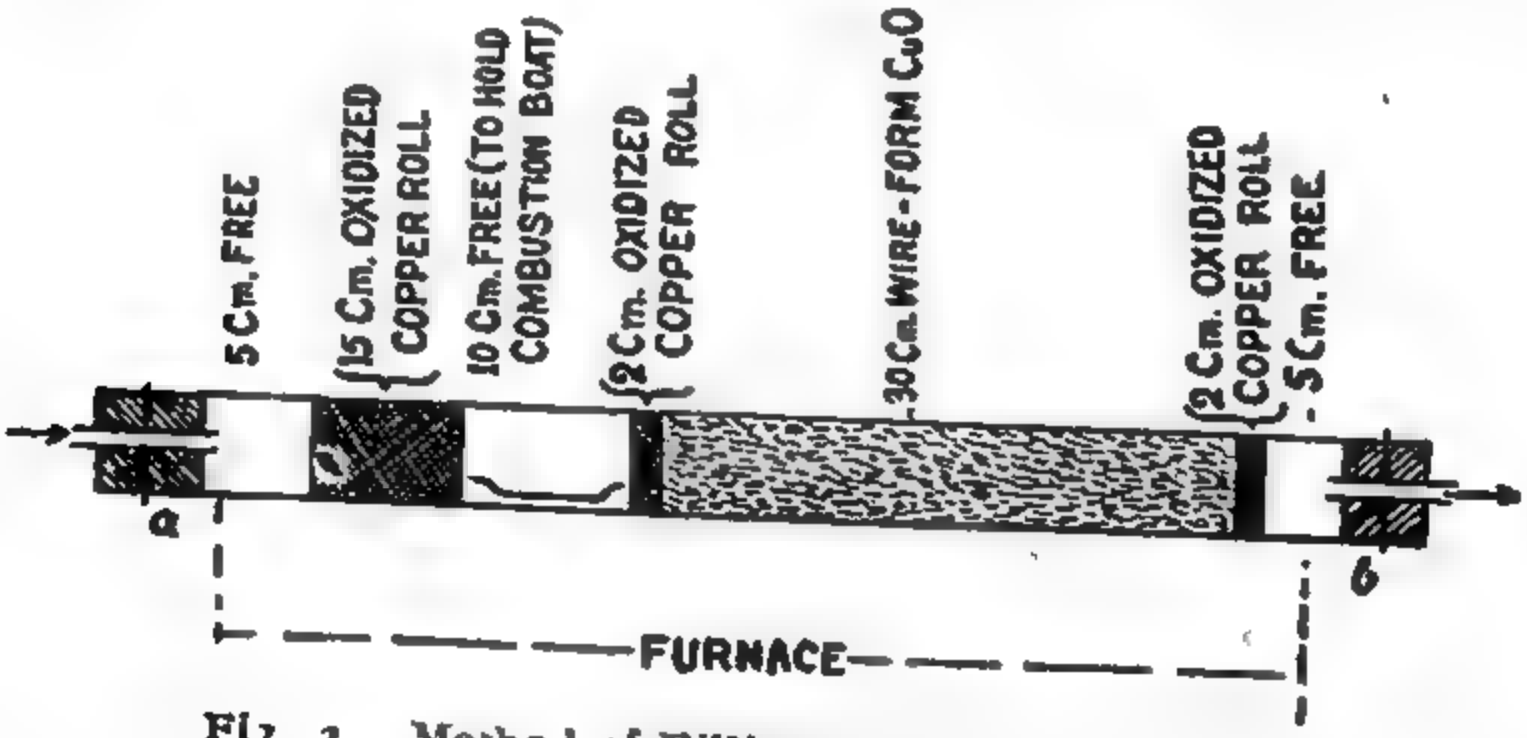


Fig. 2. Method of Filling the Combustion Tube.

(2) Two towers, one containing solid potassium hydroxide and the other fused calcium chloride, connected to each reservoir. These serve to free the oxygen and air from moisture and carbon dioxide.

[1] The ratios 2/18 and 12/44 follow from the formulae H_2O and CO_2 respectively.

(3) A bubbler containing a few drops of concentrated sulphuric acid, which serves to show the rate at which the air or oxygen is being passed through the apparatus.

(4) The combustion tube, properly filled (as shown in detail in Fig. 2) and placed in a combustion furnace.

(5) Calcium chloride U-tube for catching the water produced during the combustion of the substance

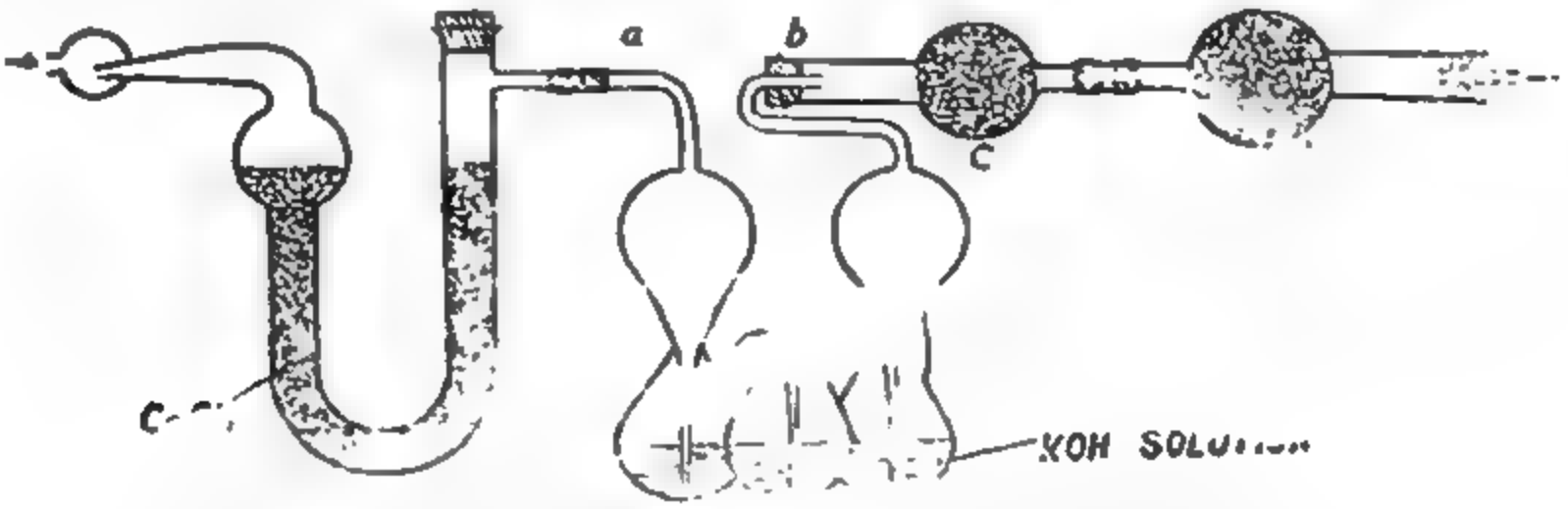


Fig. 3. Absorption Apparatus and Guard-tube.

(6) Potash bulbs containing a concentrated solution of potassium hydroxide, for absorbing the carbon dioxide produced.

(7) A Guard-tube containing calcium chloride, which serves to protect the absorption apparatus from atmospheric moisture.

The parts (5), (6), and (7) of the apparatus are shown in detail in Fig. 3.

The method of calculation will be clear from the following example.

JEAN BAPTISTE ANDRE DUMAS
(1800—1884)

The well-known French chemist who discovered the method for the estimation of nitrogen that goes by his name.

Example 1. *On combustion, 0·210 gm. of an organic compound gave 0·307 gm. of carbon dioxide and 0·127 gm. of water. What is the percentage of carbon and of hydrogen in the compound?*

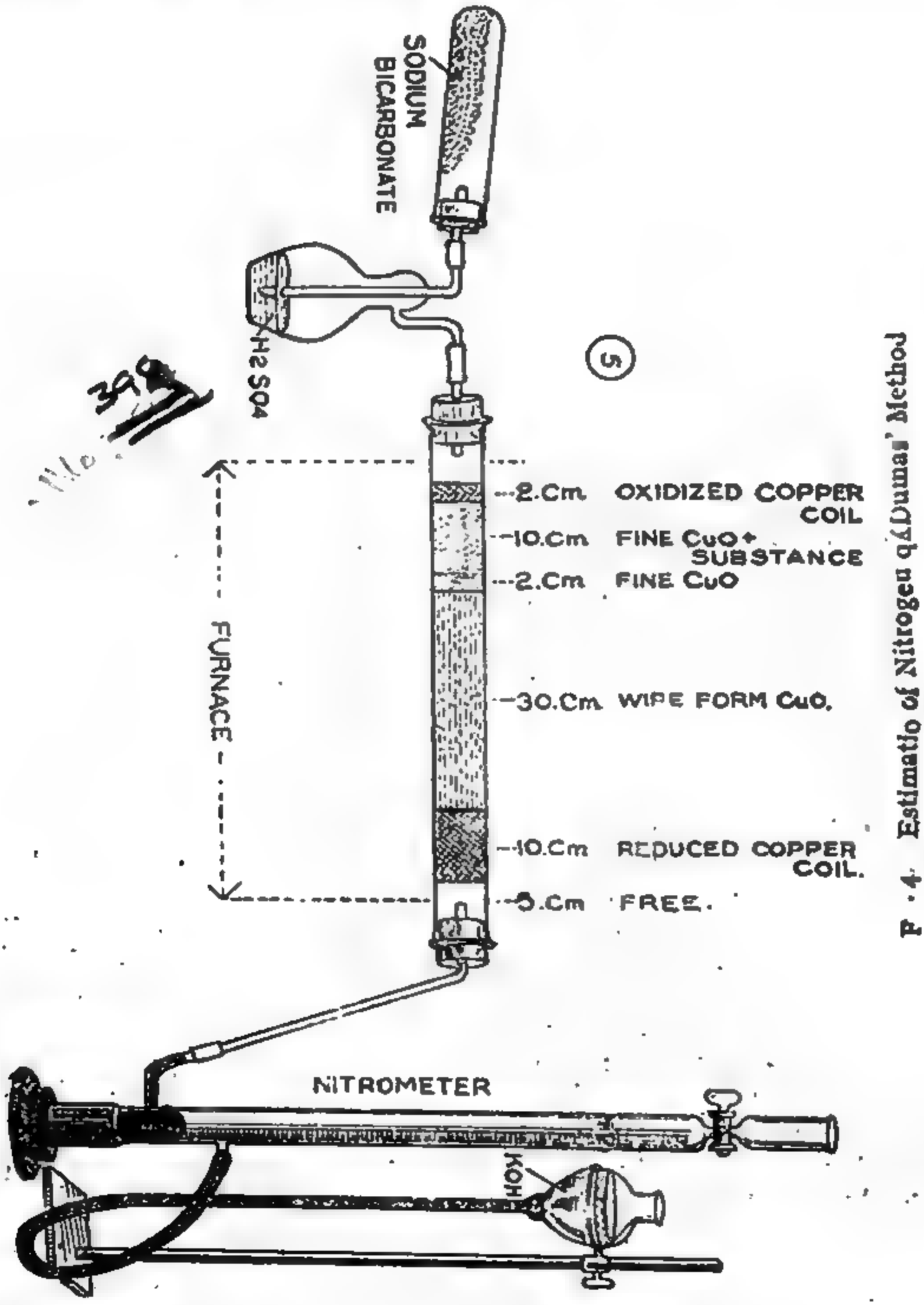
Wt. of carbon in 0·307 gm. of $CO_2 = 0{\cdot}307 \times \frac{12}{44}$ gm.

$\therefore$ Percentage of carbon $= 0{\cdot}307 \times \frac{12}{44} \times \frac{100}{0{\cdot}210} = \mathbf{39{\cdot}9}$

Wt. of hydrogen in 0·127 gm. $H_2O = 0{\cdot}127 \times \frac{2}{18}$ gm.

$\therefore$ Percentage of hydrogen $= 0\ 127 \times \frac{2}{18} \times \frac{100}{0{\cdot}210} = \mathbf{6{\cdot}7}$.

3. Estimation of Oxygen.—There is no direct method for the estimation of this element. Its amount in an organic substance is always found by *difference* (See Sec. 3, Chap. 3).



4. Estimation of Nitrogen —There are two different methods in general use for the estimation of this element—

decomposing any oxides of nitrogen formed by passing the gases over a heated spiral of bright metallic copper, and collecting the nitrogen over a strong solution of potassium hydroxide, which serves to absorb the carbon dioxide produced. From the volume of dry nitrogen, reduced to N.T.P., the weight of the gas is calculated.

The apparatus employed in this method is shown in Fig. 4. It consists of :—

(*i*) a combustion tube open at both ends,

(*ii*) a CO_2 generator, which generally consists of a hard glass tube charged with sodium bicarbonate,

(*iii*) a nitrometer, which consists of a graduated glass tube, provided at the top with a funnel and a tap, and at the base with a mercury trap and a levelling bulb,

(*iv*) a "bubbler," *i.e.*, a small size gas-washing bottle containing some concentrated sulphuric acid, which is interposed between the CO_2 generator and the combustion tube, and serves to show the rate at which the gas is passing.

Example 2. *0·188 gm. of an organic compound gave, on combustion, 31·8 ml. of moist nitrogen measured at 14°C and 758 mm. pressure. What is the percentage of nitrogen in the compound ? (Aqueous tension at 14°C = 12mm.)*

Volume of dry nitrogen reduced to N.T.P.

$$= 31{\cdot}8 \times \frac{273}{273+14} \times \frac{758-12}{760} \text{ ml.} = 29{\cdot}7 \text{ ml.}$$

Now, 22·4 litres of nitrogen at N.T.P. weigh 28 grams.

∴ Weight of 29·7 ml of nitrogen at N.T.P.

$$= 28 \times \frac{29{\cdot}7}{22{\cdot}4 \times 1000} = 0{\cdot}0371 \text{ gm.}$$

Percentage of nitrogen in the compound

$$= 0{\cdot}0371 \times \frac{100}{0\ 188} = \mathbf{19{\cdot}7.}$$

(2) **Kjeldahl's Method.** This method consists in heating a known weight (about 0·5 gm.) of the substance with concentrated sulphuric acid and postassium sulphate in a long-necked, round bottom flask of resistance glass, *A* (Fig. 5). The potassium sulphate serves to raise the boiling point of the liquid, and thus facilitates the oxidation of the substance by sulphuric acid. Under these conditions, carbon and hydrogen of the substance get oxidized to carbon dioxide and water respectively, while the nitrogen is converted into ammonia, which combines with the excess of the acid present to form ammonium sulphate. After the reaction is over (indicated by the dark coloured reaction mixture going colourless), the mixture is distilled with an excess of sodium hydroxide solution and the ammonia set free is estimated by absorbing it in a measured excess of a standard acid (Fig. 5, *B*). The excess of the acid in conical flask is then titrated with N/10 sodium hydroxide, using methyl orange as indicator

The method of calculating the result will be clear from the following example :—

the percentage of nitrogen in the substance.

14·0 ml. of N/10 NaOH are equivalent to 14·0 ml. of N/10 H_2SO_4.

∴ Volume of N/10 H_2SO_4 neutralized by ammonia

$$= 50 - 14{\cdot}0 \text{ ml.} = 36{\cdot}0 \text{ ml.}$$

36·0 ml. of N/10 $H_2SO_4 \equiv$ 36·0 ml. of N/10 NH_4OH.

Now, 1 litre of normal NH_4OH contains 14 gm. of combined nitrogen.

∴ Weight of nitrogen contained in 36·0 ml. of N/10 NH_4OH

$$= 14 \times \frac{1}{10} \times \frac{36{\cdot}0}{1000} \text{gm.} = 0{\cdot}0504 \text{ gm.}$$

Hence, the percentage of nitrogen in the substance

$$= 0{\cdot}0504 \times \frac{100}{0{\cdot}442} = 11{\cdot}4.$$

5. Estimation of Halogens (Carius' Method).—The estimation of a halogen by this method is carried out by heating the substance with fuming nitric acid in the presence of a few crystals of silver nitrate in a sealed tube Carbon and hydrogen are oxidized to carbon dioxide and water while the halogen forms silver halide, which is collected, washed, dried and weighed.

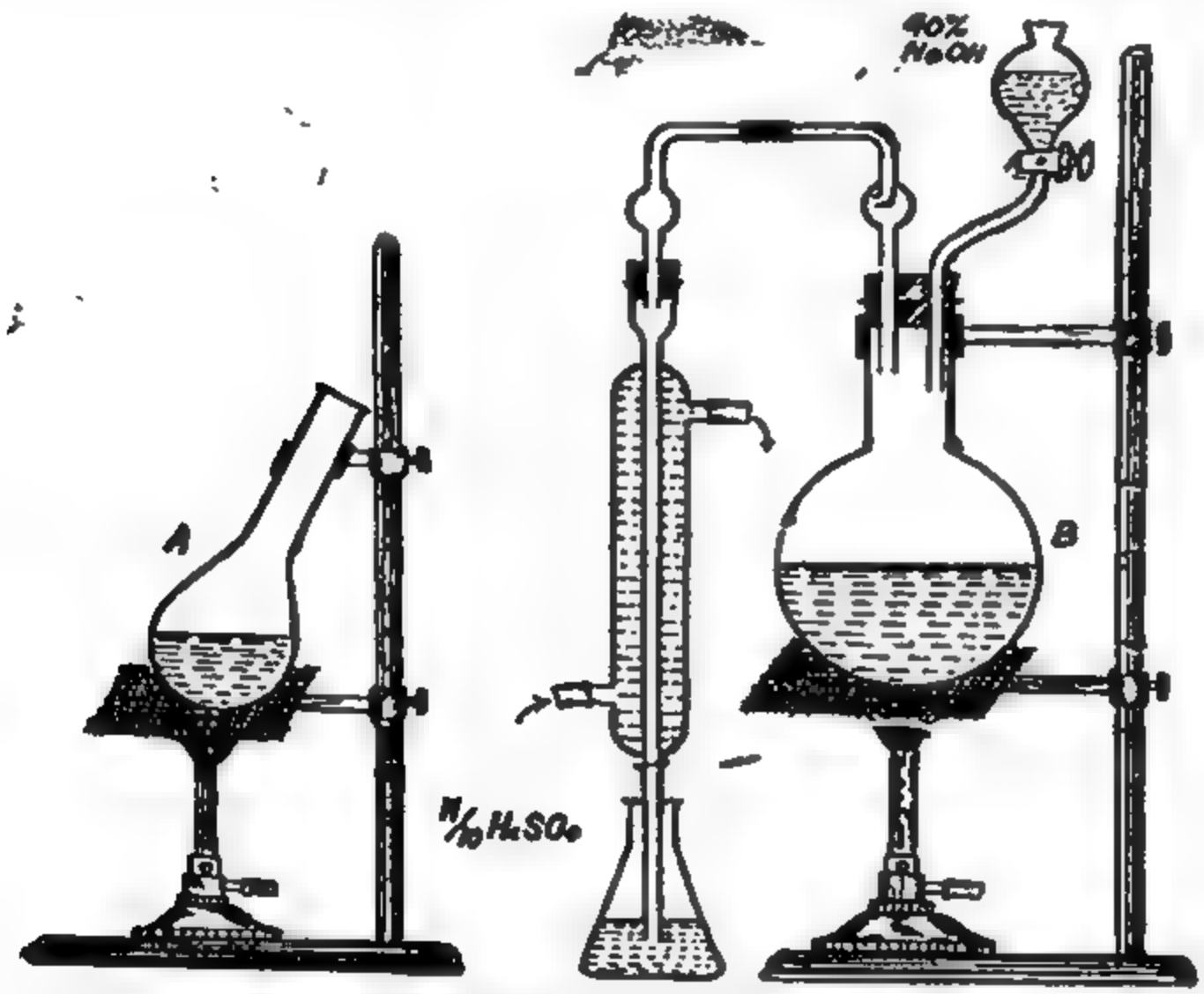


Fig. 5. Kjeldahl's Method for the Estimation of Nitrogen.

The estimation is carried out in a "bomb tube"—a special Jena glass tube with thick walls to withstand pressure. About half a gram of powdered silver nitrate and about 4 ml. of pure fuming nitric acid (sp. gr. 1·5) are placed in the tube and then a small narrow test tube containing an accurately weighed quantity (about 0 2 gm.) of the substance is allowed

Fig. 6. Carius' Tube.

to slide down into the inclined bomb tube. The test-tube will stand in the acid with its open end clear (Fig. 6). The upper end of the bomb tube is then carefully sealed off, and the tube is wrapped in asbestos paper and heated in a bomb furnace (Fig. 7) at 150°—200°C for about 6 hours. When the furnace is quite cold, the capillary end of tube is carefully opened, and the contents washed out into a beaker by means of distilled water. The precipitate of silver halide is separated, dried, and weighed.

Example 4 *0·369 gm. of a substance gave 0·568 gm. of AgBr Find the percentage of bromine in the substance.*

Since molecular weight of silver bromide, AgBr, is 108+80 or 188, 188 parts of the salt contain 80 parts of bromine.

∴ Quantity of bromine in 0·568 gm. of AgBr

$$=0{\cdot}568\times\frac{80}{188}\text{gm}$$

Hence the percentage of bromine in the substance

$$=0{\cdot}568\times\frac{80}{180}\times\frac{100}{0{\cdot}369}=\mathbf{65\ 5}.$$

6 Estimation of Sulphur and Phosphorus (Carius' Method).—The estimation of these two elements is carried out in a manner similar to that employed in the case of halogens, but without the addition of silver nitrate. Sulphur and phosphorus get oxidized to sulphuric acid and phosphoric acid respectively. These are estimated as barium sulphate and ammonium phosphomolybdate as in inorganic analysis.

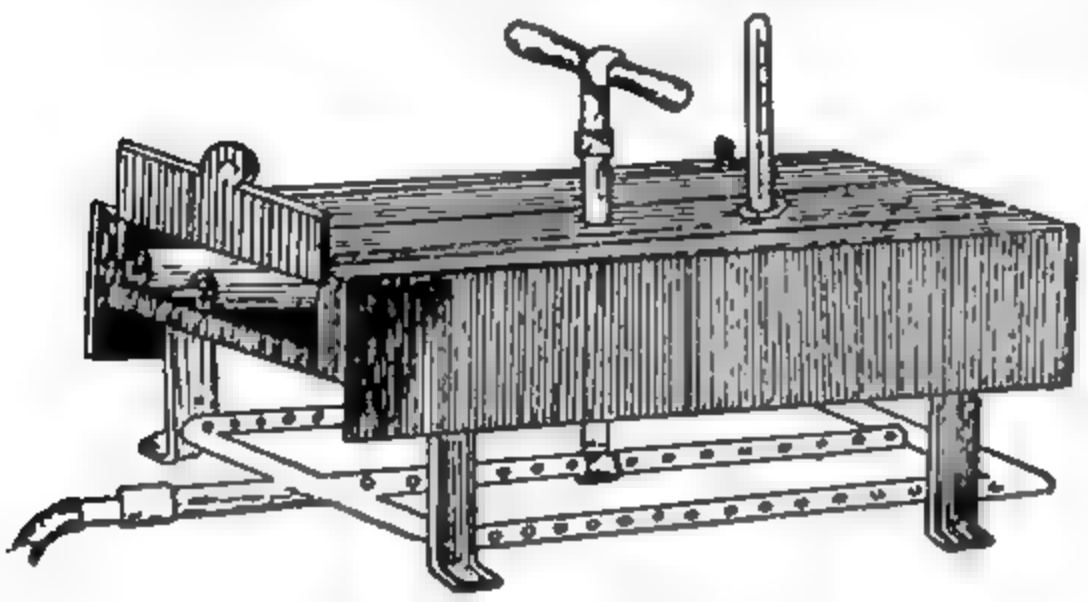


Fig. 7. Bomb Furnace.

QUESTIONS

1. Describe, with the help of a diagram, the method of estimating carbon and hydrogen in an organic compound, indicating clearly the method of filling the combustion tube.

0·20 gm. of an organic monobasic acid gave on combustion 0·505 gm. of CO_2 and 0·0882 gm. H_2O. 0·183 gm. of the acid required 15 ml. of N/10 caustic soda solution for neutralization. Calculate the molecular weight and the molecular formula of the (*Ans.* 122 ; $C_7H_6O_2$)

2. How would you estimate the percentage of nitrogen in an organic compound? 0·1475 gram of a substance containing nitrogen was distilled into 50 ml. of N/10 HCl and the excess of the acid required 25 ml. of N/10 alkali for exact neutralization. Calculate the percentage of nitrogen in the substance. (*Punjab, Inter., 1933.*)
(*Ans.* 23·7 %)

3. Calculate the percentage of nitrogen estimated by Kjeldahl's method from the following data :—

1.525 gm. of the substance was decomposed and distilled with caustic soda and the ammonia collected in 30 ml. of normal hydrochloric acid. The acid then required 120 ml. of decinormal caustic soda solution for neutralization. (*Punjab, Inter., 1938*)
(*Ans.* 16·53%)

4. 0·2 gram of an organic substance containing nitrogen was treated in such a way that the whole of its nitrogen was converted into ammonium sulphate. The whole of this was then boiled with an excess of strong caustic soda solution, and the ammonia evolved was completely absorbed in 50 ml. of N/1·5 sulphuric acid

solution The whole of this partially neutralized acid was then made up to 500 ml. 25 ml. of the latter solution required for neutralization 15 ml of N/10 caustic soda solution. Find the percentage of nitrogen in the compound.

(Na = 23; S = 32; Cl = 35·5)

(Ans. 23·3%) *(United Prov., Inter., 1951*

5 Explain Carius' method as applied in quantitative analysis of organic compounds What elements may be estimated by this method?

(Punjab, Inter. 1928

CHAPTER 5

DETERMINATION OF EMPIRICAL AND MOLECULAR FORMULÆ

1. Calculation of Empirical Formula—From the percentage composition of the substance, determined as given in the last chapter, the empirical formula, which is the simplest expression of the ratio of the atoms of different elements present in the molecule is calculated as follows :—

(1) The percentage of each element is divided by its atomic weight to get the *relative* number of atoms of the various elements present.

(2) The quotients thus obtained are then simplified by dividing them by the lowest value.

(3) The figures obtained either already are, or may be reduced to, whole numbers, which express the simplest ratio of atoms of the various elements present.

Example 1. *The analysis of a substance containing carbon, hydrogen and oxygen, gave the following results:—*

C = 68·84%; H = 4·92%; and O by difference = 26·24%

Calculate the empirical formula.

Dividing the percentage of each element by its atomic weight, we get the atomic ratio :

$$C = \frac{68{\cdot}84}{12} = 5{\cdot}74$$

$$H = \frac{4{\cdot}92}{1} = 4{\cdot}92$$

$$O = \frac{26{\cdot}24}{16} = 1{\cdot}64$$

Dividing by the smallest number, 1·64, we get the simplest atomic ratio : C = 3·5, H = 3, O = 1. Hence the empirical formula of the substance is $C_7H_6O_2$.

2. Determination of Molecular Formula.—To determine the molecular formula of a substance we must know : (1) the empirical formula, and (2) the molecular weight. The molecular weight is divided by the empirical formula weight to get the nearest whole number. The empirical formula is then multiplied by this number to get the molecular formula.

To take a specific example, analysis shows the empirical formula of acetic acid to be CH_2O. Its molecular weight is found to be 60. We have,

$$(CH_2O)_n = 60 \text{ ; whence } n = 2.$$

The molecular formula of acetic acid is therefore, $(CH_2O)_2$ or $C_2H_4O_2$.

The molecular weights of organic compounds are almost invariably

3. Molecular Weights of Volatile Substances.—From Avogadro's hypothesis it follows that equal volumes of different gases or vapours under similar conditions of temperature and pressure possess weights in the ratio of their molecular weights (since the number of molecules in each case is the same). Conversely, a *gram-molecule*, (*i.e.* the molecular weight expressed in grams) of *any* gas or vapour must occupy the same volume under similar conditions of temperature and pressure. The volume occupied by a gram-molecule of a gas at N.T.P. is termed the gram-molecular volume (G.M.V.), and is found to be equal to 22·4 litres. This relation is made use of for the determination of molecular weights of gases and volatile substances. Another relation that is employed for the molecular weight determination of a substance in the gaseous state is the following :

$$\text{Mol. Wt.} = \text{Vapour Density} \times 2.$$

4. Victor Meyer's Method.—In this method, a known weight of the substance is allowed to vaporize very rapidly. The vapour displaces its own volume of air which is collected over water, and measured under the atmospheric conditions of temperature and pressure.

Fig. 1.
Victor Meyer's Apparatus.

The apparatus employed is shown in Fig 1. The inner tube **A**, is thoroughly cleaned and dried, and an asbestos pad, or a little sand, is put at its bottom It is then placed in the other tube **B**, containing a liquid the boiling point of which is at least 20° higher than that of the substance whose molecular weight is to be determined. The inner tube is corked, the end of the delivery-tube is immersed under water, and the liquid in the outer tube is boiled. When the temperature has become constant (*i.e* , when no more air bubbles escape from the delivery-tube), a graduated tube G, filled with water is inverted over the end of the delivery-tube as shown in the figure. The cork is then momentarily removed, and a tiny stoppered bottle containing a weighed amount (0·1—0 3 gm.) of the substance is introduced. Since the temperature inside the tube is higher than the boiling point of the substance, the latter vaporizes rapidly, and blows the stopper out of the tiny bottle. The vapour rising up the tube, drives its own volume of air into the measuring tube. The suddenness of vaporization and the shape of the tube are responsible for the displacement of air by the vapour of the substance.

The measuring tube is now levelled in a hydrometer jar containing water, and the volume of the air is noted. The temperature of the water in the trough and the barometric pressure are also recorded.

Example 2.—

being 755 mm. Calculate the molecular weight of chloroform (Aqueous tension at 22°C = 20 mm.)

Barometric pressure = 755 mm.
Aqueous tension at 22° = 20 mm.
Pressure of dry air = 735 mm.

Volume of dry air reduced to N.T.P.

$$= 30{\cdot}5 \times \frac{273 \times 735}{295 \times 760} \text{ml.} = 27{\cdot}2 \text{ ml}$$

Hence, 0·146 gm. of chloroform, when in the state of vapour, would occupy 27·2 ml. at N.T.P. Therefore, the weight of the substance that would occupy 22·4 litres at N.T.P.

$$= 0{\cdot}146 \times \frac{22{\cdot}4 \times 1000}{27{\cdot}2} \text{gm.} = 120 \text{ gm}$$

∴ Molecular weight of chloroform = **120.**

5. Molecular Weights of Non-Volatile Substances —It is of course impossible to determine the molecular weight of a non-volatile substance (such as cane sugar) by Victor Meyer's method. In such a case the following two methods are generally used. One of these methods involves the determination of the depression of the freezing-point, and the other the elevation of the boiling point, of a pure solvent, caused by a given weight of the substance.

6. Freezing Point Method.- This method is based on the fact that *equimolecular quantities of different solutes dissolved in a given quantity of the same solvent produce the same depression* in *the freezing-point.*

The depression of the freezing-point produced by dissolving a gram-molecule of any non electrolyte in 100 grams of a given solvent is termed the molecular depression of the solvent and is denoted by K. Now, since the depression of the freezing point is proportional to the quantity of the solute present, if we determine experimentally the depression Δ, produced by s grams of the solute dissolved in 100 grams of the solvent, we can readily calculate the molecular weight, M, of the solute from the relation :

$$\frac{M}{s} = \frac{K}{\Delta}$$

The following table gives the freezing points of a few common solvents and the values of K, as determined experimentally:

Solvent	Freezing-points	Molecular depression (K)
Water ..	0 C	19
Acetic acid ..	17°C	39
Benzol ..	6°C	52
Phenol ..	40·C	75

Example 3. *2·107 and 4·655 gm. of a substance were dissolved in 100 gm. of benzene. The depression of the freezing-point were 0·348° C and*

The molecular weights of [illegible]

0·452°C, respectively. What was the molecular weight of the substance? The molecular lowering of freezing-point of benzene is 50°C.

If M is the molecular weight of the substance, we have

$$\frac{M}{s} = \frac{K}{\Delta}$$

where Δ is the depression of the freezing-point produced by s gm. of the substance dissolved in 100 gm. of the solvent. In the first experiment

$$s = 2{\cdot}167 \text{ gm.}$$
$$K = 50$$
$$\Delta = 0{\cdot}348°.$$

Substituting these values in the above formula we get:

$$M = \frac{50 \times 2{\cdot}167}{0{\cdot}348} = 311$$

Similarly, from the second experiment we have

$$M = \frac{50 \times 2{\cdot}833}{0{\cdot}452} = 313.$$

Hence, the mean value of the molecular weight of the two experiments = **312**.

7. Boiling-point Method.—As in the case of depression of freezing-point, it can be shown that *equimolecular quantities of different solutes dissolved in a given quantity of the same solvent produce the same elevation of the boiling-point.*

If M is the molecular weight of the substance, s the quantity of it in grams dissolved in 100 grams of the solvent, K the **molecular elevation** of the solvent (*i.e.*, the elevation of the boiling-point produced by dissolving a gram-molecule of any non-electrolyte in 100 gm. of the solvent), and Δ the observed elevation of the boiling-point, we have, as before :

$$\frac{M}{s} = \frac{K}{\Delta}$$

The following table gives the boiling-points and molecular elevation of the solvents ordinarily used :—

Solvent	Boiling-point	K
Water ..	100°C	5·2
Ethyl alcohol ..	78·0	11·5
Ether ..	35·6	21·1
Benzene ..	80·4	26·0
Chloroform ..	61·0	36·6
Acetone ..	56·3	17·2

Example 4. *0·562 gm. of a carefully purified substance when dissolved in 12·7 gm. of carbon disulphide ($K = 23{\cdot}7$) raised the boiling-point of the solvent by 0·784°. Calculate the molecular weight of the substance.*

The quantity, s, of the substance present in 100 gm. of carbon disulphide

$$= \frac{0{\cdot}562 \times 100}{12{\cdot}7} \text{ gm.} = 4{\cdot}42 \text{ gm.}$$

K for carbon disulphide = 23·7.

Elevation of the boiling-point, $\triangle$, caused by 4·42 gm. of the substance dissolved in 100 gm. of carbon disulphide

$$=0\ 784°.$$

If M is the molecular weight of the substance we have

$$\frac{M}{s}=\frac{K}{\triangle}$$

$$M=\frac{23\cdot7\times4\cdot42}{0\cdot784}=134.$$

8. Determination of Molecular Formula by Chemical Methods. Excepting the method given below for the determination of molecular weight of a gaseous hydrocarbon, no purely chemical method is known by which the molecular weight of a substance can be established with certainty ; all that we might do is to obtain information respecting the minimum value of the molecular weight or its reacting weight The following are some important cases where chemical methods are helpful :—

(1) **Gaseous Hydrocarbons.** The molecular formula of a gaseous hydrocarbon can be determined as follows, no previous quantitative elementary analysis being necessary :—

(*i*) A known volume of the gas enclosed in an eudiometer tube is mixed with a *known excess* of oxygen, and the mixture exploded. Carbon and hydrogen of the hydrocarbon burn to produce carbon dioxide and water vapour. The residual gas is allowed to cool, in order permit the condensation of water vapour, and then its volume is noted.

(*ii*) A strong solution of potassium hydroxide is now introduced into the eudiometer tube, which absorbs the carbon dioxide. When the absorption is complete, the volume of the gas (unused oxygen) is again noted.

From the volume of carbon dioxide produced from one volume of the hydrocarbon the number of carbon atoms in the molecule of the hydrocarbon is calculated with the help of Avogadro's hypothesis. The number of hydrogen atoms in the molecule is then found from the amount of oxygen used up in the production of water.

Example 5. *10 ml. of a gaseous hydrocarbon and 45 ml. of oxygen were enclosed in a eudiometer over mercury and exploded. After explosion and cooling, the volume of gases was reduced to 35 ml. On addition of caustic soda there was further reduction to 15 ml. What is the composition of the hydrocarbon ?* (*Punjab, Inter., 1922*)

Volume of the hydrocarbon taken = 10 ml.
" " " CO_2 produced = 35—15 or 20 ml.
" " " O_2 used up = 45—15 or 30 ml.

We see that 1 volume of the hydrocarbon gives on oxidation 2 volumes of CO_2. Hence, by Avogadro's hypothesis, 1 molecule of the hydrocarbon gives 2 molecules of CO_2. It, therefore, contains two atoms of carbon.

One volume of the hydrocarbon is oxidized by 30/10 or 3 volumes of oxygen. Hence by Avogadro's hypothesis, one molecule of the hydrocarbon requires for its oxidation 3 molecules of oxygen Out of these, 2 molecules must have been used up for oxidizing the two

atoms of carbon present in the molecule and the remaining 1 molecule to burn the hydrogen to water. Now, one molecule of oxygen can oxidize two molecules of hydrogen to water.

$$2H_2 + O_2 \rightarrow 2H_2O$$

Hence, a molecule of the hydrocarbon contains four atoms of hydrogen.

∴ Formula of the hydrocarbon is C_2H_4.

(2) **Organic Acids**. There exists the following relation between the molecular weight of an acid, its equivalent weight and basicity :

$$\text{Mol. Wt.} = \text{Eq. Wt.} \times \text{Basicity.}$$

Hence, the determination of the molecular weight of an acid involves the determination of (*i*) its basicity, and (*ii*) its equivalent weight. The basicity of an organic acid may be found by a study of its salts and esters. Thus, acetic acid gives rise to only one series of salts and esters. It must, therefore, in all probability, be a monobasic acid. Tartaric acid forms two potassium salts, a normal potassium tartrate and an acid potassium salt. It appears, therefore, to be dibasic.

The equivalent weight of an organic acid may be determined either volumetrically or gravimetrically. In the volumetric method a suitable known weight of the acid is titrated against standard barium hydroxide, using phenolphthalein as the indicator. The result is calculated as in Example 7 given below.

The gravimetric method for the determination of the equivalent weight of an acid involves the preparation of a pure sample of its silver, calcium or barium salt. The salt is then analysed to find the amount of the metal contained in a given weight of it. Silver salts are preferred for the equivalent weight determination, as they can be readily obtained pure and anhydrous, and are easily decomposed by heat to give metallic silver. A suitable quantity of the acid is dissolved in a slight excess of dilute ammonia. The excess of ammonia is then boiled off and to the neutral solution thus obtained is added a slight excess of silver nitrate The precipitate of the silver salt is washed and dried. A known weight of the salt is then carefully heated in a crucible so as to decompose it until a constant weight is obtained. From the weight of silver salt taken and that of silver left behind the equivalent weight of the acid is calculated as in Example 6 given below.

Example 6. *On combustion, 0·20 gram of a dibasic organic acid gave 0·040 gram of water and 0·195 gram of carbon dioxide. It contained no nitrogen. When 0·500 gram of its silver salt was ignited, it gave a residue of 0·355 gram of metallic silver. Find the empirical and molecular formulæ of the acid. (Punjab, Inter., 1944)*

Empirical formula of the acid calculated as in Example 1, comes to CHO_2.

$$\text{The Equivalent weight of the silver salt} = \frac{0{\cdot}500}{0{\cdot}355} \times 108 = 152.$$

Hence, the Equiualent weight of the acid $= 152 - 108 + 1 = 45$.

And since the acid is dibasic, the molecular weight is 90, which is twice the empirical formula weight. Hence, the molecular formula of the acid is $C_2H_2O_4$.

Example 7. *An organic monobasic acid gave the following combustion data :—*

0·100 gm. gave 0·2525 gm. of CO_2 and 0·0432 gm. of H_2O. 0·122 gm. of the acid required 10 ml. of N/10 barium hydroxide solution

for neutralisation. What is the formula of the acid ?
(Punjab, Inter , 1931)

The percentage composition of the given acid is :

$$C = 0{\cdot}2525 \times \frac{12}{44} \times \frac{100}{0{\cdot}100} \text{ or } 68{\cdot}9$$

$$H = 0{\cdot}0432 \times \frac{2}{18} \times \frac{100}{0{\cdot}100} \text{ or } 4{\cdot}8$$

$$O = 100 - (68{\cdot}9 + 4{\cdot}8) = 26{\cdot}3.$$

Dividing the percentage of each element by its atomic weight, we get the atomic ratio :

$$C = \frac{68{\cdot}9}{12} \text{ or } 5{\cdot}74;\ H = \frac{4{\cdot}8}{1} \text{ or } 4{\cdot}8;\ O = \frac{26{\cdot}3}{16} \text{ or } 1{\cdot}65;$$

Dividing by the smallest figure, 1·65, we get the simplest atomic ratio :

$$C = 3{\cdot}48,\ H = 2{\cdot}91,\ O = 1.$$

Hence, the empirical formula of acid is $C_7H_6O_2$.

Empirical formula weight = 84 + 6 + 32 or 122.

Now, quantity of the acid neutralized by 10 ml. of N/10 $Ba(OH)_2$ = 0·122 gm.

∴ Quantity of the acid neutralized by a litre of normal $Ba(OH)_2$ solution, *i.e.*, the equivalent weight of the acid

$$= 0{\cdot}122 \times 100 \times 10 \text{ or } 122.$$

Since the acid is monobasic, its molecular weight is 122, which, as we have seen above, is also its empirical formula weight. Hence the molecular formula of the acid is $C_7H_6O_2$.

As the acid is monobasic, and contains therefore only one carboxyl group, its constitutional formula must be $C_6H_5.COOH$.

(3) **Organic Bases**. Most organic bases combine with hydrochloroplatinic acid, H_2PtCl_6, giving sparingly soluble platinichlorides. The general formulæ of the platinichlorides derived from mono- and di-acid bases are respectively $B'_2H_2PtCl_6$ and $B''H_2PtCl_6$ where B' and B'' represent one molecule of the monacid and the di-acid base. On being cautiously heated, the platinichlorides decompose, leaving a residue of metallic platinum. Since the atomic weight of platinum is 195, the weight of the platinichloride that yields this amount of the metal represents its molecular weight. If the acidity of the base is known, its molecular weight can be calculated as in the following example.

Example 8. *A monacid organic base gave the following results on analysis :—*

0·100 gm. gave 0·288 gm. CO_2 and 0·0756 gm. water.
0·200 gm. gave 21·8 c.c. of nitrogen at 15°C and 760 mm.
0·400 gm. of the platinichloride left on ignition, 0·125 gm of platinum. (Pt = 195)
What is the molecular formula of the base ?
(Punjab, Inter.. 1944)

The empirical formula of the base calculated as in the previous examples comes to C_7H_9N.

If *B* is the molecular formula of the base, the formula of the platinichloride should be $B_2H_2PtCl_6$. A gram molecule of the platinichloride would leave on ignition 195 grams of pure platinum. Hence, the molecular weight of the platinichloride $B_2H_2PtCl_6$

$$= 0{\cdot}400 \times \frac{195}{0{\cdot}125} \text{ or } 624$$

∴ Molecular Weight of the base B

$$= \frac{624-(2+195+213)}{2} = 107.$$

This is identical with the empirical formula weight. Hence, the molecular formula of the base is the same as its empirical formula, *i.e.*, C_7H_9N.

QUESTIONS

1. What is the difference between the *empirical formula* and the *molecular formula ?* How will you proceed to establish the empirical formula of a substance ?

2. How is the molecular formula of a *volatile* organic substance determined ?

3. On combustion, 0·152 gram of a non-nitrogenous organic compound gave 0·304 gram of carbon dioxide and 0·124 gram of water. The vapour density was found to be 45·3. Determine its molecular formula.

[*Ans.* $C_4H_8O_2$.] (*Punjab, Inter., 1927*)

4. 0·3696 gm. of a compound containing C, H and O gave on combustion 0·5420 gram CO_2 and 0·2168 gram H_2O. Find its simplest formula and state whether this formula is necessarily the same as the molecular formula, giving reasons for your answer. [*Ans.* CH_2O.] (*Unit. Prov., Inter, 1922*)

5. An organic compound was found to contain 66·6% carbon and 7·4% hydrogen. 0·135 gm. of the same substance on analysis gave 27·9 c.c. of nitrogen at N. T. P. If its molecular weight be 108, calculate the formula of the compound.

[*Ans.* $C_8H_9N_2$] (*Unit. Prov., Inter., 1928*)

6. An organic substance, containing C, H, and N, gave the following results on analysis: 0.465 gm. of it yielded on combustion 1·32 gm. of CO_2 and 0·315 gm. of H_2O. 0·2325 gm. of the substance yielded 27·8 ml. of Nitrogen at N.T.P. Calculate the formula of the substance. [*Ans.* C_6H_7N.] (*Unit. Prov., Inter., 1934*)

7. Describe briefly a simple method for the determination of the composition of a gaseous hydrocarbon.

12·5 ml. of a gaseous hydrocarbon was mixed with 48 ml. of oxygen, the mixture ignited by an electric spark. On cooling, there was a contraction of 25 ml., and, on treating the remaining gas with caustic potash solution, there was a further contraction of 12·5 ml. Find the molecular formula of the hydrocarbon.

(*Punjab, Inter., 1947*)

8. 12 ml. of a gaseous hydrocarbon were mixed with 90 ml. of oxygen, and the mixture exploded. After explosion, the volume was 72 ml. On adding KOH, 36 ml. of gas disappeared, leaving oxygen only. What is the molecular formula of the gas ? All the above measurements were made at 15°C. and 755 mm. pressure, the gases being saturated with moisture. [Aq. tension at 15°C=12.7 mm.] [*Ans.* C_3H_6.] (*Punjab, Inter., 1919*)

9. (*a*) How would you estimate the percentage of nitrogen in an organic compound ?

(*b*) 0·20 gram of an anhydrous acid gave, on combustion, 0·040 gram H_2O and 0·195 gram CO_2. The acid is found to be dibasic, and 0·5 gram of the silver salt leaves, on ignition, 0 355 gram silver. What is its molecular formula ? (Ag=108)

[*Ans.* $C_2H_2O_4$] (*Punjab, Inter., 1940*)

10. Describe Carius' method for the estimation of halogens.

A substance gave the following results on analysis :—

0·2 6 gm. gave 0·264 gm CO_2 and 0.126 gm. water. Also 0.369 gm. of the substance gave 0·568 gm. silver bromide. What is the empirical formula of the substance ? [*Ans.* C_3H_7Br] (*Punjab, Inter., 1929*)

11. On combustion 0·324 gm. of an anhydrous dibasic acid containing only C, H and O gave 0.3168 gm of CO_2 and 0·0648 gm. of H_2O. 0·50 gm. of its silver salt on ignition gave 0·355 gm of metallic silver. Calculate the empirical formula of the acid, and give its constitutional formula.

[Ag=108]

(*Punjab, Inter., 1943*)

CHAPTER 6

MOLECULAR STRUCTURE AND ISOMERISM

1. Isomerism. Among inorganic compounds the empirical formula is, in almost all cases, sufficient to characterize the substance in hand. Thus there is but one substance having the formula $CuSO_4$, only one having the formula HCl, and so on In organic compounds, on the other hand, even the molecular formula is not sufficiently characteristic to eliminate the possibility of confusion with other compounds. There may be many organic compounds having exactly the same molecular formula, which nevertheless differ from one another in their phasical and chemical properties. Such compounds are called **isomers** or *isomerides*, the phenomenon being termed *isomerism*.

There are, for example, two different compounds having the molecular formula C_2H_6O, five having the formula C_3H_8O, and as many as eighteen having the formula C_8H_{18}. The number of isomers theoretically possible in the case of compounds having higher molecular weight may be very large indeed. Thus there are 802 possible isomers for the molecular formula $C_{13}H_{28}$. All the isomers theoretically possible in a given case, however, are aot necessarily known.

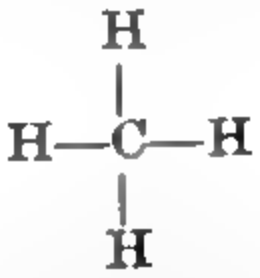
The difference in physical and chemical properties of isomeric substances is to be soughts in the internal structure of the molecule, the atoms in which, in each case, are assumed to be differently arranged.

2. Molecular Structure. In 1858, Kekule advaneed two hypotheses upon which the structural formulæ of organic compounds are based. The first of these postulated that *carbon* is *a tetravalent element* and the second that *its atoms have the capacity to link with one another*

By the aid of the above two hypotheses, it is possible to represent graphically the molecular architecture of a majority of organic compounds The combining capacity or *valency* of an atom is indicated by joining the symbols of the elements concerned in the union by the small lines or dots, so that each line or dot represents a unit of valency. It is assumed that in the formation of a compound, the valencies of the atoms undergoing combination are mutually used up. Hence, the elements which, like hydrogen, are monovalent must combine according to the formula H—X. Similarly, di-, tri- and tetravalent elements must combine with hydrogen as in the following formulae :—

Water

Ammonia



Methane

While in inorganic compounds elements do not always show the same valency, among organic compounds variable valency is rather the exception than the rule. The elements carbon, hydrogen and oxygen, of which the majority of organic compounds are composed, show, in almost all cases, a valency of four, one and two respectively

The way in which the various atoms in a molecule are linked together indicates the **structure or constitution** of the compound. It is expressed

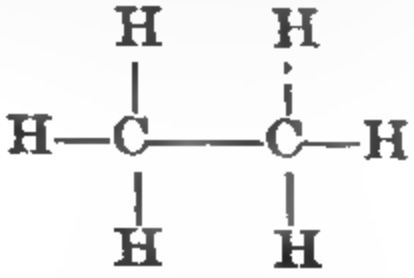
by structural or constitutional formulae. In writing the structural formulae the following rules, based on experience, are observed :—

(1) *Tetravalency of the Carbon Atom.* The carbon atom is almost invariably tetravalent, and may thus combine with at the most four univalent atoms or groups. Thus, in methane, CH_4, and carbon tetrachloride, CCl_4, one atom of carbon is combined with four atoms of hydrogen and chlorine respectively.

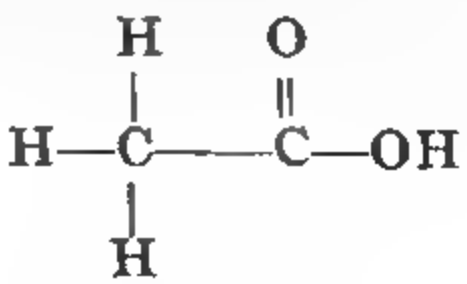
FRIEDRICH AUGUSTE KEKULE
(1829—1896)
the famous German chemist who is the founder of the Theory of the Structure of Organic Compounds.

(2) *Equivalence of the Four Carbon Valencies.* The four valencies of a carbon atom are equialent to one another, as the replacement of *any one* of the four hydrogen atoms of the methane molecule by a monovalent substituent always gives the same product.

(3) *Linking of Carbon Atoms.* Carbon atoms possess a great capacity to link with one another. In the formation of carbon links, it is assumed that each carbon atom is bound by 1, 2, or 3 valencies to a neighbouring carbon atom and the remaining valencies can then be saturated by hydrogen, oxygen, chlorine etc. Those compounds in which only singly bound carbon atoms are present are termed **saturated compounds**; *e. g.*,

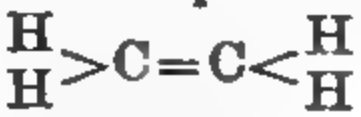


Ethane

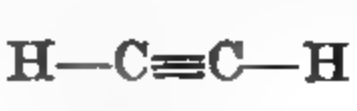


Acetic acid

while those containing carbon atoms linked by double or triple bonds are called **unsaturated compounds** : *e. g* ,

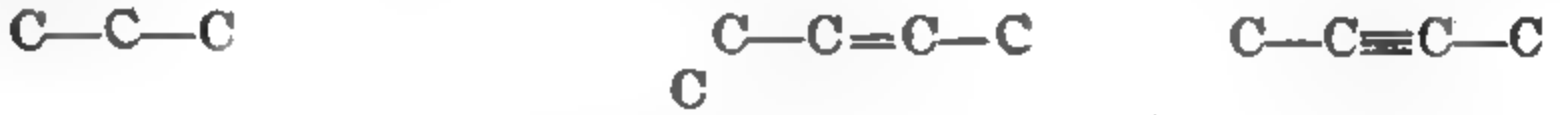


Ethylene

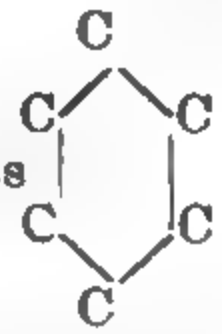


Acetylene

Similarly, three or more carbon atoms may link together, forming an open chain, such as,

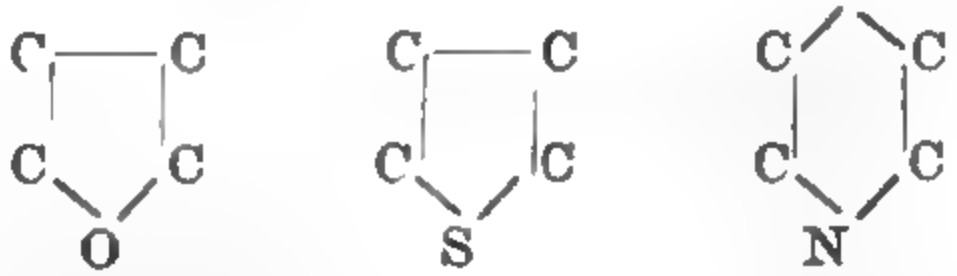


or a closed chain or ring, such as

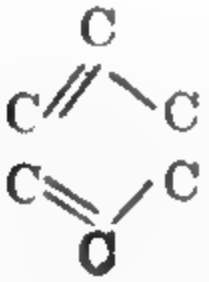


Some important open chain compounds are present in fats and oils. For this reason, the branch of organic chemistry that deals with open chain compounds is called the **fatty** or **aliphatic series** and a substance belonging to this class is known as a *fatty* or *aliphatic compound.*

Substances containing closed chains are termed **cyclic compounds.** If the rings are composed entirely of carbon atoms, they are called **carbocyclic** : if they contain, in addition to carbon, one or more atoms of some other polyvalent elements, as in the following:—

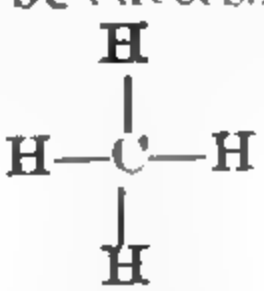


they are termed **heterocyclic.**

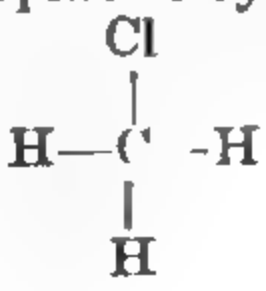


Among carbocyclic compounds, those containing rings of six carbon atoms with alternate single and double bonds, as shown in the margin, are of great importance, and are called **aromatic compounds** or *benzene derivatives.*

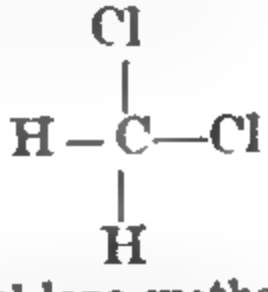
3. Substitution. The atoms of an element present in the molecule of an organic substance may be replaced or *substituted* by an equivalent number of atoms of other elements. Thus, the hydrogen atoms of methane can be successively replaced by atoms of chlorine.



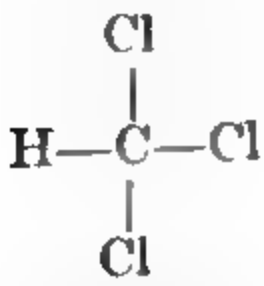
Methane



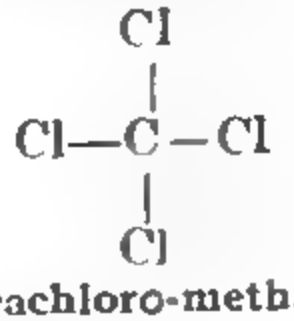
Monochloro-methane



Dichloro-methane



Trichloro-methane



Tetrachloro-methane

They may also be replaced by mono-, di- or trivalent groups.

4. Isomeric Change. Under certain conditions an organic compound may pass into another having the same atomic composition but a different structure. This type of reaction, called an **isomeric change or isomerization,** involves a *rearrangement* of the component atoms of the molecule. The most important example of an isomeric change is the conversion of ammonium cyanate into urea :

$$\underset{\text{Ammonium cyanate}}{NH_4O.C\equiv N} \longrightarrow \underset{\text{Urea}}{NH_2.CO.NH_2}$$

5. Metamerism. This term refers to a kind of structural isomerism which exists between substances of the same class, and is due to the linking of different alkyl radicals to the same polyvalent atom or group. Metamerism is exhibited by ethers, ketones, esters, amines, etc. The following few cases may be mentioned as illustrations of this type of isomerism :—

$C_4H_{10}O$:—

$\begin{matrix}CH_3\\C_3H_7\end{matrix}>O$ — Methylpropyl ether

$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O$ — Diethyl ether

$C_5H_{10}O$:—

$\begin{matrix}CH_3\\C_3H_7\end{matrix}>CO$ — Methylpropyl ketone

$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>CO$ — Diethyl ketone

$C_3H_6O_2$:—

$CH_3COO\,CH_3$ — Methyl acetate

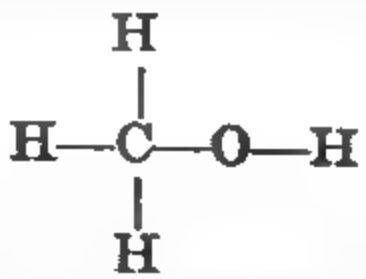
$HCOOC_2H_5$ — Ethyl formate

6. Determination of Structural Formula. After the molecular formula of a substance has been found as given in Chapter V, the organic chemist proceeds to determine the structure of the molecule. This may involve the following steps :

(1) First, writing down all the possible combinations of the constituent atoms, consistent with their respective valencies

(2) Then, from the various possible formulæ thus obtained, selecting one that agrees best with the properties of the compound and its methods of formation.

In case the number of atoms in the molecule is small, the determination of its constitution is usually a simple matter. Thus, if the valencies of carbon, hydrogen and oxygen be assumed to be 4, 1, and 2 respectively, the compound having the molecular formula CH_4O (**methyl alcohol**) can have only one structure as shown below :

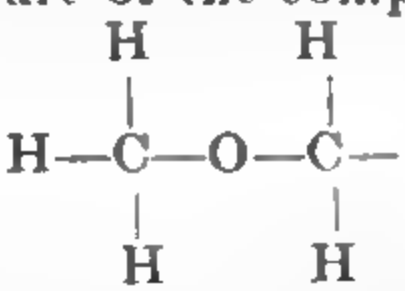
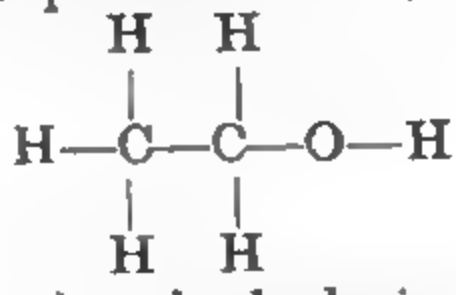


Similarly, the compound of the molecular formula CH_2O (formaldehyde) must have the structure $H.C\leqslant^{H}_{O}$. In case two or more structural formulæ are possible, we must select the right one by refrence to the following points :—

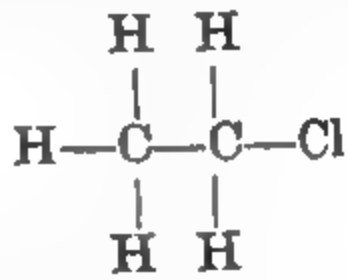
(i) The possibility of the compound being transformed into, or of its being produced from, compounds of known structure. We know it from experience that *when an atom or radical present in a*

molecule is replaced by another substitutent, the latter, as a rule, goes into the position originally occupied by the former.

The procedure may be illustrated by reference to **ethyl alcohol,** C_2H_6O. As one may see by trial, there are only two ways in which the structure of the compound may be represented *viz.*,

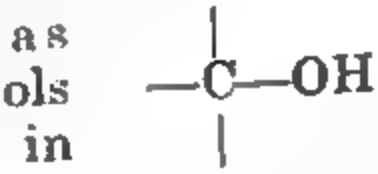
(a)  and (*b*) 

Now, ethyl alcohol may be obtained by the hydrolysis of ethyl chloride, C_2H_5Cl, and, conversly, it may be converted into ethyl chloride by treatment with hydrogen chloride. Hence, its structure must be analogous to that of ethyl chloride. But, there is only one structure possible for the latter substance, shown in the margin. Hence, ethyl alcohol must possess the constitution (*b*) and not (*a*).



The conclusion thus arrived at is in complete harmony with the chemical behaviour of ethyl alcohol. Thus, of the six hydrogen atoms that the molecule contains only *one* is replaceable by sodium ; hence this hydrogen atom must be in a different state of combination from the rest. This condition is fulfilled by the formula that we have just now selected.

(*ii*) The close similarity of the physical and chemical properties of the compound with those of another whose constitution is known. Thus, an additional proof of ethyl alcohol as possessing the structure (*b*) is that in its entire physical and chemical behaviour, it closely resembles methyl alcohol, for which there is only one structure possible, *viz.*, CH_3OH. Hence, ethyl alcohol must contain a hydroxyl group in its molecule, just as methyl alcohol does. Similarly, all other alcohols must have in their molecules the grouping shown in the margin.



(*iii*) The formula finally adopted must be supported by as many reactions of the compound as possible. It must also be checked by reference to its various physical properties. As the last step, an attempt is made to **synthesize** the compound from one of known structure by a series of simple reactions that the formula under cosideration may suggest. Should this be successful, the formula is finally accepted as established.

7. Systematic Investigation of an Organic Substance. We may here summarize the different steps in the systematic investigation of an unknown organic compound. They are :

(1) Purification.

(2) Qualitative elementary analysis.

(3) Quantitative elementary analysis and calculation of the empirical formula.

(4) Determination of the class to which the compound belongs by applying characteristic tests for each class.

(5) To study the properties of the compound and to deduce therefrom the constitutional formula.

When once the class to which the compound belongs is known, it is quite simple to investigate its chemical properties and write its constitutional formula.

(6) Synthesis of the compound, by simple chemical reactions in order to confirm the constitutional formula deduced in step 5

8. Structure of the Atom. The atoms of all elements have been built by Nature from the same three kinds of primary particles, called the *electrons*, the *protons* and the *neutrons* The **electron** carries a unit negative charge, and its mass is 1/1840th of that of the hydrogen atom. The **proton** carries one unit of positive charge, and has practically the same mass as that of an atom of hydrogen The **neutron** has the same mass as the proton, but is electrically neutral (hence the name).

The electrons, the protons and the neutrons are not jumbled together in a haphazard way in the atom but are arranged according to definite scheme. In the centre of the atom there is a very dense, heavy body, called the **nucleus**, which is a compact structure consisting of all the protons and the neutrons that the atom contains The number of protons in the nucleus of an atom represents the **nuclear charge,** which always corresponds to the **atomic number** of the element, i. e. its position in the periodic table.

While the number of protons in the nucleus of the atom of a given element is always the same, the number of neutrons varies within certain limits Thus we get atoms of the same element possessing different masses. These are called the **isotopes**. There exist three isotopes of hydrogen having a mass equal to 1, 2 and 3 units, which are called *protium* (or simply hydrogen), *deuterium* and *tritium* respectively. The nuclei of all the three kinds of hydrogen atoms have one proton in each case. But the number of neutrons with which the proton is associated is zero, one and two respectively- Like hydrogen, all other elements have been shown to consist of mixtures of isotopes. Hence, the *atomic weight* of an element is comparatively of little importance. In fact, it has no physical signifiance, but is merely the *average* mass of the atom of an element.

9. Arrangement of Electrons. All the electrons in an atom revolve round the nucleus, each in its own specific orbit. The various electronic orbits are grouped into a number of **shells**, depending on the energy possessed by the electrons concerned. The maximum number of electronic orbits that a given shell can accomodate is given by the expression $2n^2$, where n is the shell number, counting from the innermost. The first shell, therefore, can accomodate 2 electrons. the second 8, the third 18 and the fourth 32. The outermost shell of an atom cannot, however, acquire more than 8 electrons and the next-to-the-outermost not more than 18.

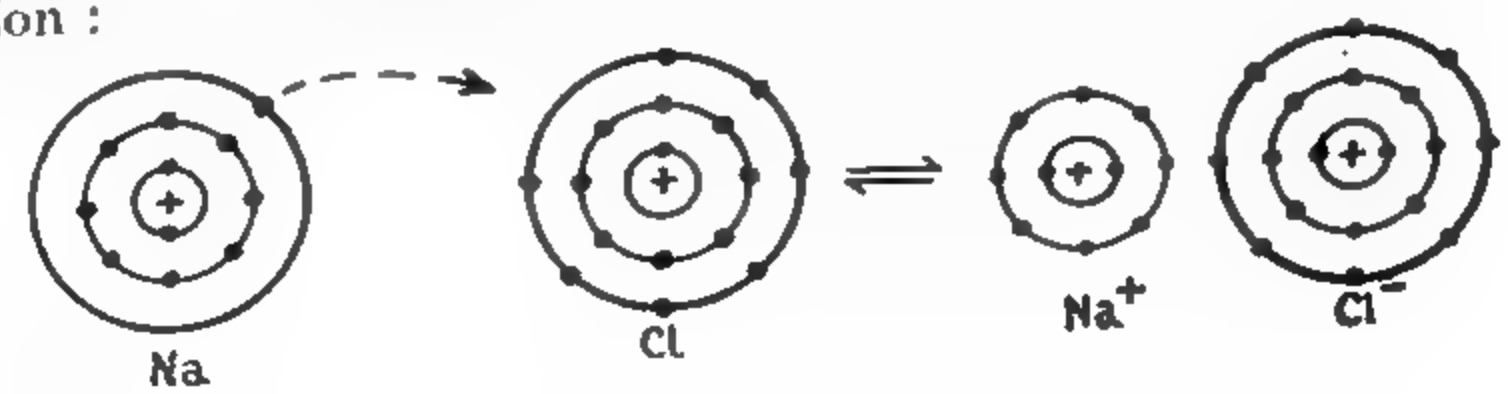
Starting from the hydrogen atom, which consists of a single electron going round a one-proton nucleus, the evolution of the atom takes place in 92 steps. At each step, one proton is added to the nucleus and one electron into one of the electronic shells. These 92 steps represent the various atomic numbers. Hydrogen, the first element of the periodic table has the atomic number 1, while the atomic number of uranium, the last element of the periodic table, is 92.

The electronic configuration of the elements of the first three periods of the periodic table is given below :—

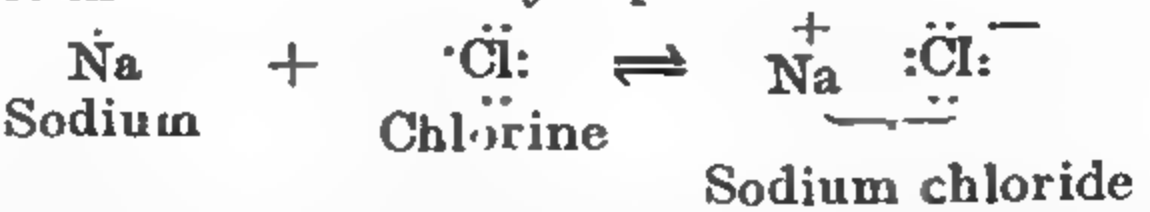
Period	Element	At. No.	Number of electrons in various shells: 1st. shell	2nd shell	3rd shell
I	Hydrogen	1	1	..	..
	Helium	2	2	..	..
II	Lithium	3	2	1	..
	Beryllium	4	2	2	..
	Boron	5	2	3	..
	Carbon	6	2	4	..
	Nitrogen	7	2	5	..
	Oxygen	8	2	6	..
	Fluorine	9	2	7	..
	Neon	10	2	8	..
III	Sodium	11	2	8	1
	Magnesium	12	2	8	2
	Aluminium	13	2	8	3
	Silicon	14	2	8	4
	Phosphorus	15	2	8	5
	Sulphur	16	2	8	6
	Chlorine	17	2	8	7
	Argon	18	2	8	8

10. Electronic Theory of Valency. When different elements are brought together, their atoms may combine to form compounds. The combining capacity of atoms is termed **valency.** According to modern theory, the development of valency by an atom depends on the number of electrons in the outermost shell, or the "valency shell", of the atom. The key to the problem of valency is provided by the elements of the helium family (zero group of the periodic table). The atoms of these elements possess no power to combine with other atoms, and are, therefore, supposed to possess maximum stability of the valency shell. The helium atom has 2 electrons in the valency shell, while all the other members of this group have 8. Atoms of all elements tend to have a complete shell of 8 electrons (except hydrogen and helium which can have a maximum of 2). It is this tendency of the atom that is responsible for chemical combination. The completion of the valency shell may be achieved by an atom by borrowing, lending or sharing of electrons The borrowing or lending of electrons gives rise to *electrovalency* (Sec. 11), while sharing results in the development of *covalency* (Sec. 12).

11. Electrovalency. Union between two atoms may take place by the *transfer* of electrons from the outermost shell of the one to that of the other. Thus, when a chlorine atom having 7 valency electrons combines with a sodium atom having one such electron, the electron from the latter atom is transferred to the chlorine atom Both the atoms now have a stable arrangement of 8 electrons in their outermost shells. Further, the transfer of an electron from the sodium to the celorine atom makes the former acquire a unit positive charge, and the latter a unit negative charge. These charged atoms or *ions* hold each other by mutual attraction :

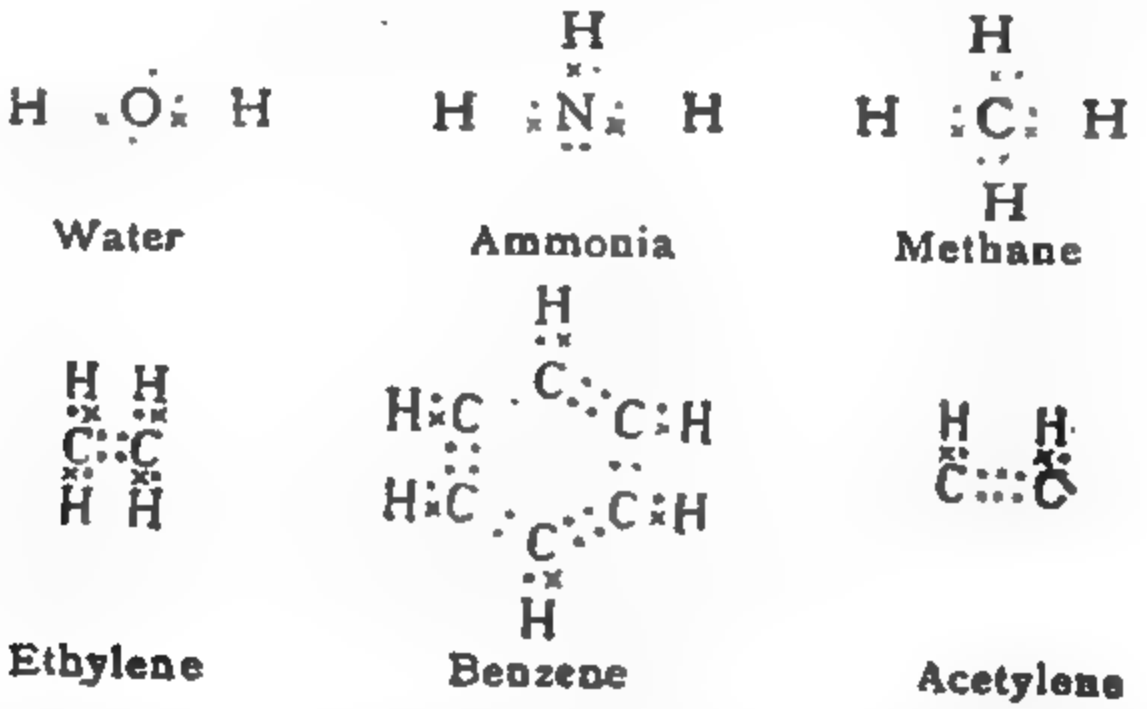


The change is most conveniently represented as follows :—



A compound formed as above is termed an **electrovalent compound** or *polar compound*. The latter name refers to the fact that the molecule of such a compound has a positive and a negative pole, and consequently, under suitable conditions, has a tendency to break up into positive and negative ions. The combination of the above type, called an *electrovalency* is found chiefly among acids, bases and salts.

12. Covalency. In this type of union the atoms combine by *sharing* one, two, or three pairs of electrons with each other so as to complete their octets. In each pair of shared electrons one is contributed by each atom. One pair of shared electrons corresponds to a **single bond**, two pairs to a **double bond**, and three pairs to a **triple bond**. A covalent bond is non-ionizable. The following are some examples of covalent compounds :



The **co-ordinate link** is similar to the covalent link except that *both* the electrons constituting the bond are supplied by *one* of the atoms. Thus, in the nitro-group, —N(=O)→O one of the oxygen atoms is linked to the nitrogen atom by a covalent double bond and the other by a *co-ordinate* link. The latter link is symbolized by a small arrow pointing from the nitrogen to the oxygen atom. This shows that the two electrons reqired for the formation of the link are supplied by the *nitrogen* atom.

13. Valency of Hydrogen and Oxygen. The hydrogen atom has only one electron. When this is lost, we get the hydrogen ion, H^+, which is the common constituent of all acids. In organic compounds, hydrogen forms a single covalency, *i.e.* a 2-electron link, as in methane, H:C(H)(H):H

The oxygen atom has six electrons in the valency shell. It may acquire two more from another atom, giving rise to the oxide ion, O^{--}. In the case of organic compounds, oxygen acts as a bicovalent element. In

methyl alcohol, $H:\ddot{\underset{\ddot{H}}{\underset{|}{C}}}:\ddot{O}:H$, for example, oxygen has two single bonds, one with carbon and the other with hydrogen. The two oxygen atoms of acetic acid, $CH_3.C\overset{O}{\underset{OH}{\diagup\!\!\diagdown}}$, are both bicovalent. One of them is bound on the one hand with carbon and on the other with hydrogen, a single covalency being developed in each case. The other oxygen atom is bound to the carbon atom by a double bond, *i.e.* a 4-electron link. In all these cases, the oxygen atom fills up its valency shell completely. That is, its valency shell acquires 8 electrons, which is the maximum that it can hold.

14. Valency of Carbon. The carbon atom has 4 electrons in the valency shell, and the opposing tendencies to gain and borrow electrons are so well balanced that the atom practically never develops an electrovalency, either positive or negative. The only mode of combination that carbon atom exhibits is by the exercise of covalencies. Like all other atoms, it tends to have a complete set of 8 electrons in the valency shell. As it already has 4, it will combine wieh four mono-covalent atoms, as in the case of methane, $H:\ddot{\underset{\ddot{H}}{\underset{|}{C}}}:H$.

Combination between two carbon atoms may be effected through a single bond (as in ethane, H_3C-CH_3), a double bond (as in ethylene, $H_2C=CH_2$), or a triple bond (as in acetylene, $HC\equiv CH$). This power of carbon atoms to get linked together to form long chains and rings is most remarkable and unique.

15. Valancy of Nitrogen. The nitrogen atom has 5 electrons in the valency shell, and readily develops a tricovalency, as in ammonia, $H:\ddot{\underset{\ddot{H}}{\underset{|}{N}}}:H$ or amines, $R:\ddot{\underset{\ddot{H}}{\underset{|}{N}}}:H$, etc. It is also capable of developing a tetra-covalency, as in the case of the ammonimum ion, $\left\{\begin{array}{c}H\\ H:\ddot{N}:H\\ \ddot{H}\end{array}\right\}^+$ and the nitro-group, $N\overset{O}{\underset{O}{\nearrow\!\!\!=}}$, One of the nitrogen-oxygen bonds in the latter is a normal double bond and the other a co-ordinate link (see Sec. 12) As the valency shell of the nitrogen atom cannot accommodate more than eight electrons, the maximum covalency of nitrogen, like that of carbon, is four.

QUESTIONS

1. Give the different steps in the systematic investigation of the formula of an organic compound. *(Punjab Inter., 1927)*
2. Write an account of Keklue's theory of molecular structure.
3. Write notes on (*i*) Isomerism, (ii) Intramolecular change, (*iii*) Substitution, and (*iv*) Metamerism. *(Ajmer, Inter., 1933, 1934)*

4. How is the structure of an organic substance determined? Illustrate your answer by a specific example.

5. Write an essay on "The Electronic Theory of Valency."

6. What is meant by covalent and electrovalent linkages, and which of these linkages generally occurs in organic compounds? Give the electronic formula of methane. (*Punjab, Inter., 1933*)

7. On what conceptions regarding the structure of a carbon atom, is the graphic formula of an organic compound based? Point out its limitations. Describe the electronic structure of a carbon atom, and write down the electronic formulae of the following: Methane, Ethylene, Chloroform, and Carbon Tetrachloride. (*Punjab Inter. 1945*)

8. Explain the main postulates of kekule's theory of molecular structure in terms of the electronic theory of valency.

9. "The *valency* of hydrogen, oxygen and chlorine in organic compounds is 1, 2 and 1 respectively". What is the significance of this statement from the view point of modern theory?

10. "While carbon is consistently tetra-covalent, nitrogen may act as a tri-covalent or a tetra- covalent element". Why is it so?

PART II

ALIPHATIC OR OPEN-CHAIN COMPOUNDS

CHAPTER 7

SATURATED HYDROCARBONS OR PARAFFINS

1. Methane, CH_4. Methane is one of the hydrocarbons, *i.e.*, compounds of Carbon with hydrogen It is the parent hydrocarbon of the aliphatic series of carbon compounds.

Occurrence Methane is produced in considerable quantities when cellulose and other organic matter undergoes putrefaction under stagnant water On this account, the gas is found in marshy places; hence the name **marsh gas**. The *natural gas* that issues from the earth in petroleum districts consists of methane and its homolegues. Methane also issues from seams in coal mines, where, by diffusing into the air, it forms an explosive mixture; hence the name *fire damp* given to it by coal-miners. Methane is an important constituent of *coal gas* of which it constitutes between 30 and 40 per cent.

Preparation. (1) Methane is most conveniently prapared in the laboratory by heating fused sodium acetate with dry soda-lime ($NaOH + CaO$). The active constituent of soda-lime in this reaction is sodium hydroxide; but the pure alkali is not employed, owing to its being deliquescent and easily fusible.

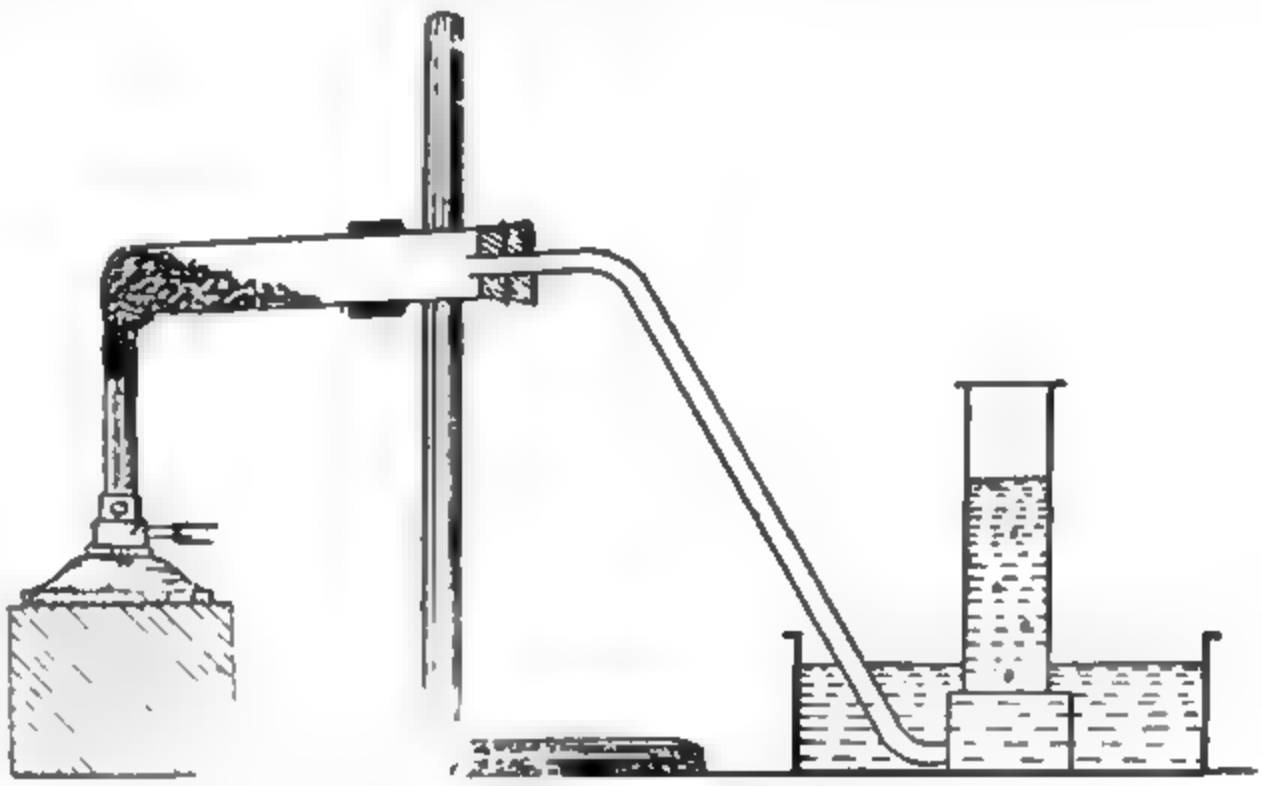


Fig. 1. Preparation of Methane.

$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$$

Expt. 1. Heat an intimate mixture of *fused*[1] sodium acetate (1 part) and dry soda-lime (4 parts) in a hard glass tube provided with a delivery tube. Collect the issuing gas over water. (*See* Fig. 1.)

(2) Another source from which methane may be obtained in the laboratory is aluminium carbide, Al_4C_3. This, when boiled with water, yields methane contaminated with hydrogen (20 per cent.) and other impurities.

$$Al_4C_3 + 12H.OH \rightarrow 4Al(OH)_3 + 3CH_4$$

(3) Pure methane is most readily obtained by the reduction of methyl iodide, CH_3I, with nascent hydrogen (usually from zinc-copper couple and alcohol) :—

[1]The fused sodium acetate is made by heating the hydrated salt in a dish, until it melts, resolidifies and melts again to a transparent mass. Strong heating must be avoided, as the salt chars at high temperatures.

$$CH_3I + zH \rightarrow CH_4 + HI$$

The details of the experiment are similar to those described for ethane in Expt. 3, Sec. 3.

Synthesis[1]. Methane has been synthesized by the following reactions:—

(1) When a current of hydrogen is passed over carbon heated at 1200°, the elements combine together to yield a small proportion (1 per cent) of methane :

$$C + 2H_2 \rightleftharpoons CH_4.$$

The reaction is reversible, since when pure methane is heated at 1200°, about 99 per cent. of it is decomposed into its elements. If carbon be intimately mixed with finely divided nickel, the combination occurs at lower temperatures, and much larger amounts of methane are formed.

(2) Sabatier and Senderens have obtained an almost quantitative yield of methane by passing a mixture of hydrogen and carbon monoxide or dioxide over finely-divided nickel at 250° to 300°.

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The process has commercial possibilities in localities where natural gas is not available.

(3) The earliest synthesis of methane was effected by Berthelot by passing a mixture of carbon disulphide vapour and hydrogen sulphide over heated copper :

$$CS_2 + 2H_2S + 8Cu \rightarrow CH_4 + 4Cu_2S$$

Physical Properties. Methane is a colourless gas with a slight odour. It can be liquefied at 11° under a pressure of 180 atmospheres. it is very slightly soluble in water. 100 ml. of water at 4° dissolving 5 ml. of the gas.

Chemical Properties. Methane, like other hydrocarbons of this series, is characterized by inertness and stability. It is neutral in character, and is not affected by acids or alkalies. Nor is it affected by oxidizing agents such as nitric acid, potassium permanganate or dichromate The only important reactions of methane are :

(1) *Combustibility*. Methane burns in air with practically a non-luminous flame, forming carbon dioxide and water :

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

When mixed with air or oxygen and ignited, the gas explodes violently. Mixtures of methane and air occurring in coal-mines are of constant danger to miners.

(2) *Action with Chlorine*. Methane is a "saturated" compound, and can give rise only to substitution products. When it is mixed with chlorine or bromine vapour, there is no action in the dark. But on exposing the mixture to sunlight, an interaction occurs with explosive violence. The four hydrogen atoms of the methane molecule are successively replaced by chlorine with the production of the following four substitution products :

[1] The complete synthesis of a compound means its formation from the component elements, from simpler compounds already obtained from their elements.

Chloromethane, or methyl chloride, CH_3Cl
Dichloromethane, or methylene chloride, CH_2Cl_2
Trichloromethane, or chloroform, $CHCl_3$
Tetrachloromethane, or carbon tetrachloride, CCl_4

(3) *Action with Ozone.* When methane is treated with ozonized oxygen, two of its hydrogen atoms are exchanged for an oxygen atom, with the production of formaldehyde :

$$CH_4 + 2O_3 \rightarrow \quad H_2C{\leqslant}^{H}_{O} \quad + H_2O + 2O_2.$$

Formaldehyde

This reaction constitutes a **delicate test for methane,** since even small quantities of formaldehyde may be readily identified by certain characteristic reactions that the latter compound gives (*see* under Formaldehyde).

Expt. 2. *To study the chemical properties of methane* :

(*a*) Burn a cylinder full of methane. Notice that the flame is non-luminous. Test the gas left in the cylinder with lime water : the latter turns milky.

(*b*) Pass the gas through (*i*) bromine water, (*ii*) sodium hydroxide solution rendered pink with phenolphthalein, (*iii*) dilute sulphuric acid rendered pink with methyl orange, and (*iv*) potassium permanganate solution acidified with sulphuric acid. Notice that there is no appearance of reaction with any of these reagents

(*c*) Fill a strong "soda water" bottle one-third with methane and two thirds with oxygen, and then bring its mouth near a flame (Fig 2) A powerful and very loud explosion will occur

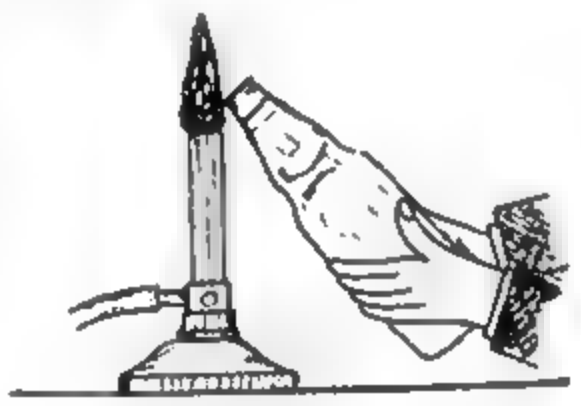
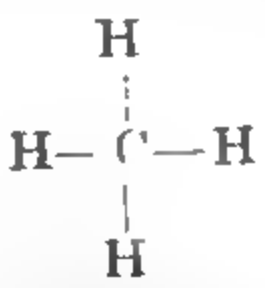


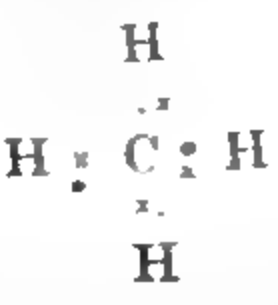
Fig 2

Composition. Methane being a gaseous hydrocarbon, its composition can be determined by the method explained in Sec 39.

Constitution. Since carbon is tetravalent and hydrogen monovalent, methane molecule must be represented by the constitutional formula shown below :

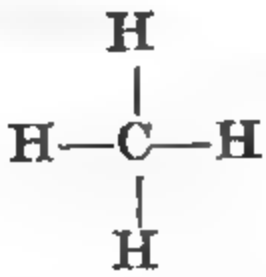


Electronic Formula. In terms of electronic theory of valency, the above formula assumes the form :



each one of the hydrogen atoms is linked to carbon by a **single bond,** in the formation of which one electron is contributed by the carbon and the other by the hydrogen atom.

Saturated Nature of Methane. The maximum valency of the carbon atom is four. In the methane molecule,



all the four valencies of the carbon atom are satisfied by four hydrogen atoms. Hence, there is but one way open for methane to form derivatives, *i. e.*, by **substitution**. For example, in the reaction with chlorine one or more halogen atoms enter the methane molecule by displacement of an equivalent number of hydrogen atoms. In this manner, we get from methane four different **substitution products** : *viz.*,

Monochloro-methane, CH_3Cl
Dichloro-methane, CH_2Cl_2
Trichloro-methane, $CHCl_3$
Tetrachloro-methane, CCl_4

A compound, like methane, in which the maximum combining capacity of carbon atoms is exerted, and which, therefore, can form derivatives only by substitution, is called a **saturated compound.**

3. Ethane, C_2H_6. Ethane occurs, along with methane, in the *natural gas*, and is also found dissolved in petroleum.

Preparation. Ethane may be prepared by methods similar to those used for methane (Sec. 50). Thus, methods (1) and (2) given below correspond to methods (1) and (3) described under methane. There are also other methods for the preparation of ethane (3, 4 and 5) which are not applicable to the preparation of methane.

(1) By heating anhydrous sodium propionate, C_2H_5COONa, with dry soda-lime :—

$$\begin{matrix} C_2H_5COONa \\ + \\ HONa \end{matrix} \rightarrow \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3.$$

(2) By the reduction of ethyl iodide, C_2H_5I, by means of zinc-copper couple and alcohol :—

$$C_2H_5I + 2H \rightarrow C_2H_6 + HI$$

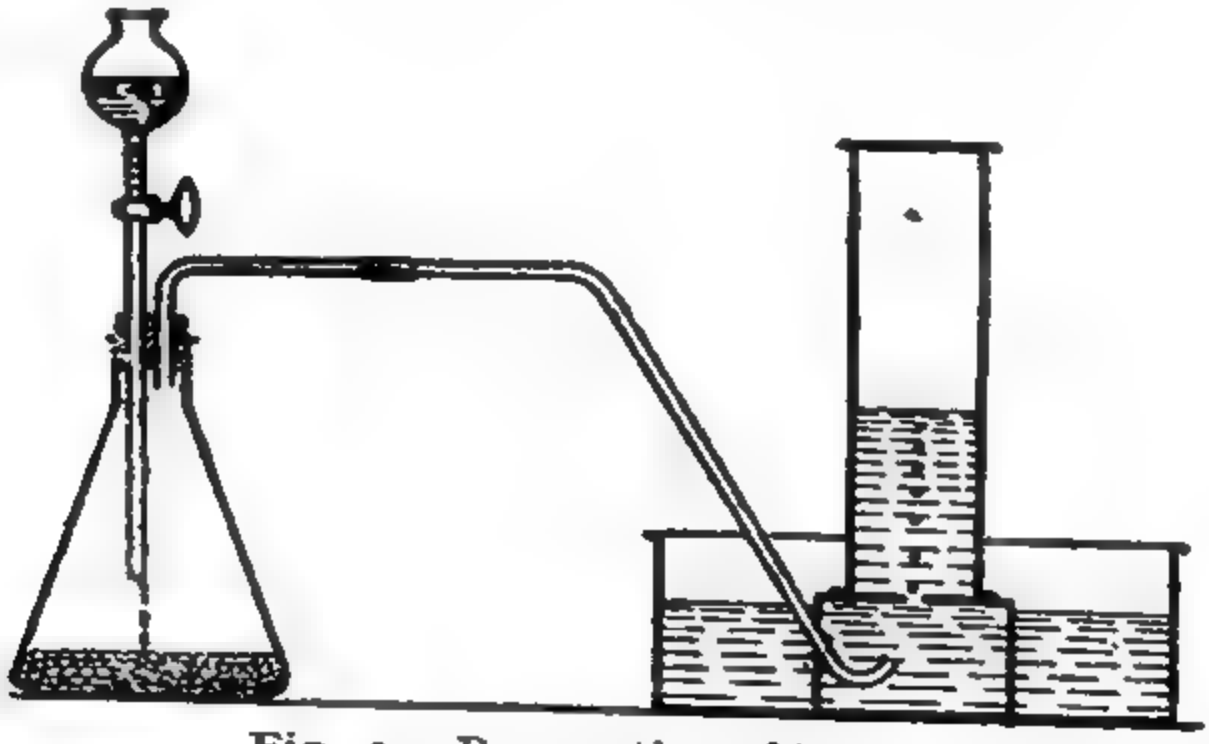


Fig. 3. Preparation of Ethane.

Expt. 3. *Preparation of Ethane from Ethyl Iodide.* Take 20 grams of granulated zinc in a beaker, and cover it with 2 per cent solution of cupric sulphate. Allow to stand, until the blue colour is discharged ; then pour off the solution. Repeat the

above treatment with cupric sulphate three or four times. Wash the zinc-copper couple, thus obtained, with water, and finally with a little alcohol. Then place it in a flask provided with a dropping funnel and a delivery tube (Fig. 3). Add to the flask 100 ml. of alcohol mixed with a drop or two of dilute sulphuric acid, and then drop ethyl iodide into the mixture from the dropping-funnel. Collect the gas evolved over water.

Study the properties of the gas as in the case of methane (Expt. 2).

(3) By heating methyl iodide, CH_3I, with metallic sodium or zinc (**Wurtz' reaction**[1]) :—

$$2CH_3I + Zn \rightarrow \underset{\text{Ethane}}{CH_3.CH_3} + ZnI_2$$

This reaction may be employed for synthesizing ethane from methane.

(4) *By Anodic Oxidation of Acetate-ion* (**Kolbe's Reaction**). When a concentrated aqueous solution of sodium or potassium acetate (or dilute acetic acid) is submitted to electrolysis in a cell divided by a porous partition, the acetate ions lose electrons to the anode (oxidation). The discharged acetate groups, being unstable, undergo decomposition so as to give ethane and carbon dioxide, which are set free at the anode :—

$$2CH_3COO^- - 2e^- \rightarrow CH_3.CH_3 + 2CO_2$$

At the same time, hydrogen is set free at the cathode, owing to the reduction of the hydrion (derived in the case of acetic acid from the acid itself and in that of potassium acetate solution from the water):—

$$2H^+ + 2e^- \rightarrow H_2$$

The arrangement of the apparatus is shown in Fig. 4.

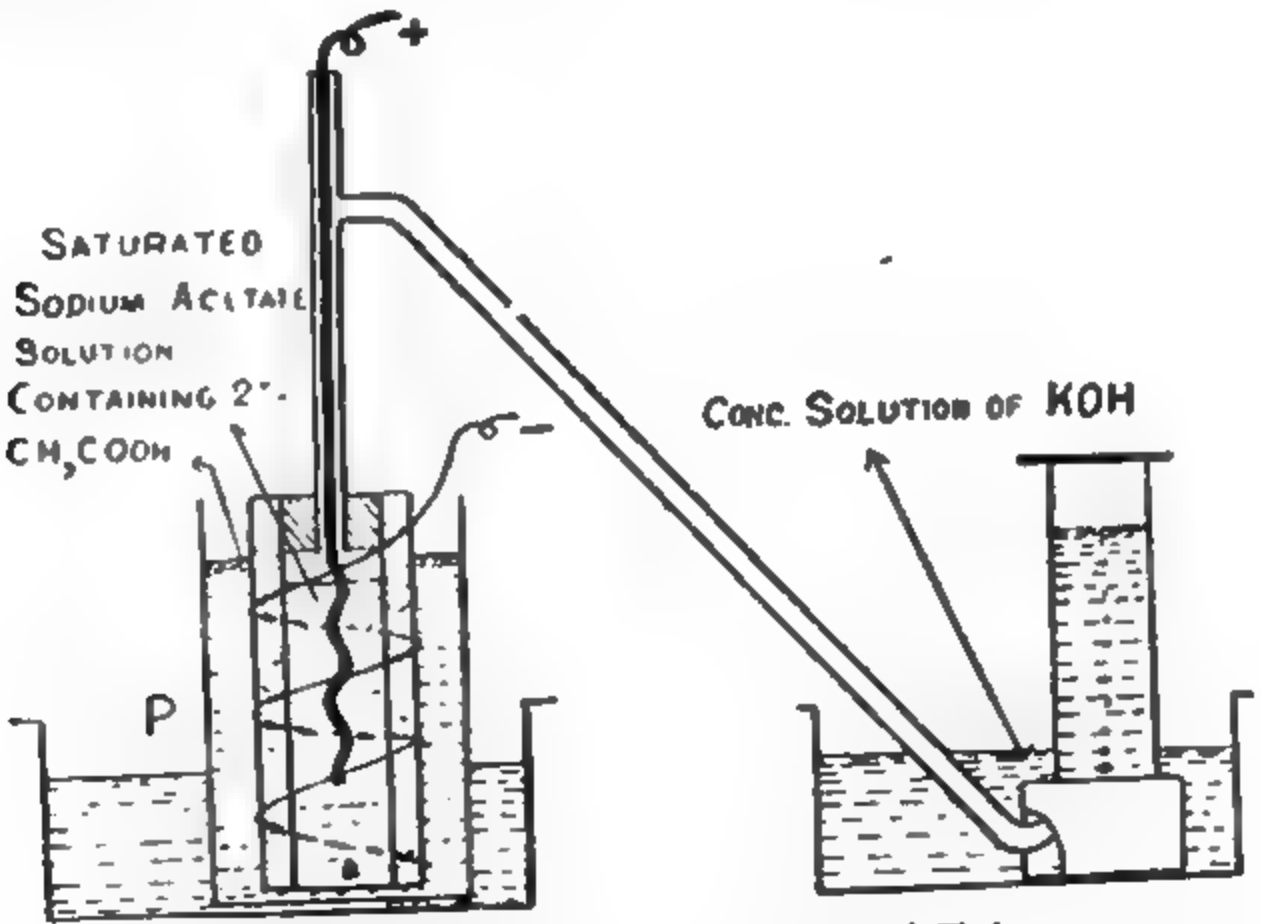


Fig. 4. Electrolytic Preparation of Ethane.

A saturated solution of sodium (or potassium) acetate (containing about 2 per cent of glacial acetic acid) is placed in the porous pot *P*. The latter is fitted with a cork carrying the T-shaped delivery tube into which is fused a stout platinum wire to act as the anode. A nickel wire, wound round the cell, serves as the cathode. The porous pot is placed in a beaker containing the same solution as the porous pot itself. The whole apparatus is placed in a trough of cold water so as to keep the temperature of the electrolyte below 20°. The gas set free

[1] **Charles Adolf Wurtz (1817—1884)** was a French chemist.

at the anode is collected over a strong solution of potassium hydroxide, which absorbs the carbon dioxide.

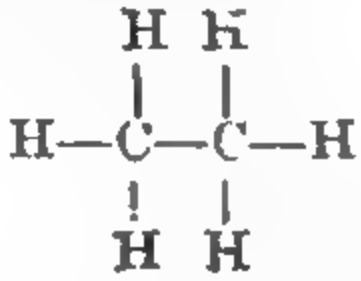
(5) Ethane has been prepared on a *large scale* by the combination of ethylene and hydrogen in the presence of finely-divided nickel.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

Properties. Ethane, like methane, is a colourless, tasteless, gas. It is practically insoluble in water and slightly soluble in alcohol.

In chemical properties, too, ethane closely resembles methane. It readily reacts with chlorine and bromine, yielding *substitution products*, 1, 2, 3, 4, 5, or 6 hydrogen atoms being replaced by an equivalent number of chlorine or bromine atoms. The *final* products are hexachloro-ethane, C_2Cl_6, and hexabromo-ethane, C_2Br_6, both of which are colourless crystalline solids.

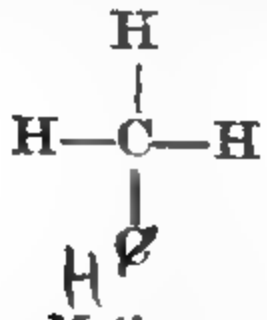
Constitution. Explosion with oxygen (Chap. 5, Sec. 8) shows that the molecular formula of ethane is C_2H_6. The two carbon atoms must be *directly* united, because a monovalent atom could not possibly link them together. Moreover, since the carbon is tetravalent, the two carbon atoms must carry three atoms of hydrogen each. Hence, the structural formula of ethane is as shown below :



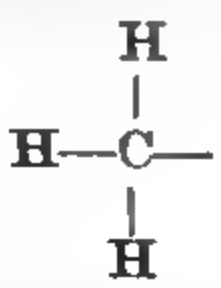
This view is confirmed by the formation of ethane from methyl iodide by Wurtz' reaction.

4. Saturated Nature of Ethane. Ethane, like methane, is a saturated compound, as the four valencies of each of the carbon atoms are fully satisfied. In the case of each carbon atom, three of the valencies are usud up in linking three hydrogen atoms, while the remaining fourth is utilized in holding the other carbon atom.

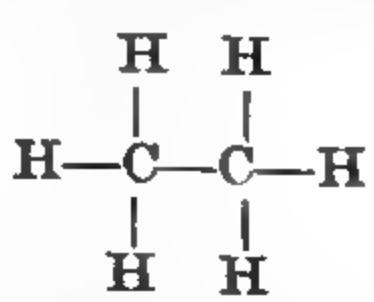
5. Structural Relationship of Methane and Ethane. If one of the hydrogen atoms of methane, CH_4, be imagined to be detached from the molecule, we will be left with a univalent group, called the **methyl group**, $-CH_3$. Such a group, however, is *not* capable of independent existence, for the fourth valency of the carbon atom seeks to be satisfied. If we try to liberate such a group from combination (as for instance, by the action of sodium or zinc on methyl iodide) two such groups will get linked together, giving a molecule of ethan, $CH_3.CH_3$. Hence, ethane must be regarded as derived from methane and may be called **methyl methane**.



Methane



Methyl group (incapable of independent existence)



Ethane or Methyl-methane

6. Homologous Series. We have seen that ethane is derived from

methane by the substitution of one of the hydrogen atoms of the latter by a methyl group. If one of the hydrogen atoms of ethane be replaced by a methyl group, we get another hydrocarbon, called *propane*, $CH_3.CH_2.CH_3$. Proceeding in the same manner, we get a series of hydrocarbons, each successive member of which has one atom ef carbon and two of hydrogen more than its predecessor :—

Methane, CH_4
Ethane, C_2H_6
Propane, C_3H_8
Butane. C_4H_{10}

If the number of carbon atcms in the molecule of any of the above hydrocabons be expressed by n, the number of hydrogen atoms will be found to be $2n+2$. This is true for the higher members as well. The series, therefore, possesses the **general formula** C_nH_{2n+2}.

Now, if we replace a hydrogen atom in each of the above hydrocarbons by a hydroxly group, we obtain the following series :—

$CH_3.OH$	$C_2H_5.OH$	$C_3H_7.OH$	$C_4H_9.OH$
Methyl alcohol	Ethyl alcohol	Propyl alcohol	Butyl alcohol

Here, also, we find that each member of the series differs from the preceding one by CH_2, and the whole series may be expressed by the general formula $C_nH_{2n+2}.OH$.

Replacement of the hydrogen of hydrocarbons by other groups or atoms always results in the formation of various series of compounds, whose successive members differ by CH_2, and which may be represented by general formulæ as in the above two cases.

A group of similarly constituted compounds, two consecutive members of which differ in molecular composition by CH_2, *is termed a* **homologous series,** *and its various members are known as* **homologues.**

The various members of a homologous series possess, owing to similar molecular constitutions, similar chemical properties ; and their physical properties have been found to undergo a gradual change from member to member. From this it is clear that if we know the various methods by which, say, methane and ethane are prepared and also their chemical behaviour, we can foretell the methods of preparation and the chemical behaviour of *any* other member of the series.

The above remarks apply equally well to other homologous series of carbon compounds. Hence, organic chemistry comprises a thorough study of the methods of preparation, reactions, and constitution of one or two *selected* members of a homologous series. Equipped with this knowledge, we can foretell the methods of preparation and chemical behaviour of any other member of the series. This fact not only simplifies the study of organic compounds, of which an almost unlimited number exists, but also makes this study highly interesting and instructive.

From what has been said above, it is also clear that the formula, the chemical properties, gradation in phyical properties, and the methods of preparation of the members of a homologous series may be stated in *general* terms. This method of treatment of the subject will be illustrated below in the case of paraffins, and will also be used for the study of other homologous series.

7. The Paraffins. Methane and its homologues are called *paraffins.*

This term refers to the inertness of the hydrocarbons of this series towards most chemical reagents (Latin, *parum*, little and *affinis*, affinity). Since they are saturated in nature, they are also called **saturated hydrocarbons.**

As already stated, the **general formula** of the paraffins is C_nH_{2n+2}. The names of the various members of this series end in *ane*, and are derived from the Greek numerals indicating the number of carbon atoms in the molecule. The following are a few of the first members of the series:—

NAME	FORMULA	NUMBER OF ISOMERIDES
Methane	CH_4	1
Ethane	C_2H_6	1
Propane	C_3H_8	1
Butane	C_4H_{10}	2
Pentane	C_5H_{12}	3
Hexane	C_6H_{14}	5
Heptane	C_7H_{16}	9
Octane	C_8H_{18}	18

Physical Properties. The physical properties of paraffin hydrocarbons show a gradual change. The first four members of the series are gaseous, while those containing from 5 to 16 carbon atoms are liquids. The higher members are colourless solids. The boiling-point rises regularly as the series is ascended, but the difference between the boiling points of consecutive hydrocarbons gradually diminishes.

General Chemical Characters. The paraffin hydrocarbons are characterized by their lack of chemical activity. They are netural in character, and are not affected by most of the reagents excepting the halogens (*see* under *Methane*). They do not react with oxygen at ordinary temperatures; but at higher temperatures, they are readily oxidized, and the oxidation, when once started, is difficult to control. It is only recently that a beginning has been made in the preparation of certain products by the direct oxidation of aliphatic hydrocarbons. Paraffins react with chlorine and bromine in the presence of sunlight to give substitution products.

General Methods of Formation. On examining the methods of preparation of methane and ethane described above, it will be clear that hydrocarbons in this series may be prepared by the following general methods:—

(1) By heating the sodium salts of carboxylic acids of the acetic series with soda-lime ; *e.g.*,

$$\underset{\text{Sodium acetate}}{CH_3.COONa} + NaOH \rightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(2) By the electrolysis of aqueous solutions of potassium salts of

acids of the acetic series (**Kolbe's Reaction**). This method is described in detail in the case of ethane on p. 52.

(3) By the reduction of an alkyl halide with zinc-copper couple and alcohol ; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \rightarrow \underset{\text{Ethane}}{C_2H_6} + HI$$

(4) By heating alkyl halides with metallic sodium or zinc (**Wurtz' reaction**) *e.g.*.

$$\underset{\text{Methyl iodide}}{2CH_3I} + Zn \rightarrow \underset{\text{Ethane}}{CH_3.CH_3} + ZnI_2$$

If a mixture of two different alkyl halides is used in this reaction, three different hydrocarbons are produced at the same time. Thus, a mixture of methyl iodide and ethyl iodide yields ethane, propane and butane as shown below:

$$2CH_3I + Zn \rightarrow \underset{\text{Ethane}}{C_2H_6} + ZnI_2$$

$$2C_2H_5I + Zn \rightarrow \underset{\text{Butane}}{C_4H_{10}} + ZnI_2$$

$$\begin{matrix} CH_3I \\ + \\ C_2H_5I \end{matrix} + Zn \rightarrow \underset{\text{Propane}}{C_3H_8} + ZnI_2$$

(5) By the hydrogenation of an unsaturated hydrocarbon in the presence of finely-divided nickel (**Sabatier and Senderens' reaction**) :—

$$\underset{\text{Etnylene}}{H_2C=CH_2} + H_2 \rightarrow \underset{\text{Ethane}}{H_3C.CH_3}$$

$$\underset{\text{Acetylene}}{HC \equiv CH} + 2H_2 \rightarrow \underset{\text{Ethane}}{H_3C.CH_3}$$

Note. Methods 2, 4 and 5 *cannot* be used for the preparation of methane. This is because methane molecule contains only one carbon atom. Methods 2 and 4 are not applicable for methane, because they involve the linking together of two or more carbon atoms ; reaction 5 cannot be used because no unsaturated hydrocarbon is known which contains less than two carbon atoms.

8. Propane, $CH_3.CH_2.CH_3$.

Occurrence. This hydrocarbon also occurs in natural gas.

Preparation. Propane may be prepared in the laboratory by any of the following methods :-

(1) By heating sodium butyrate with soda-lime :-

$$\underset{\text{Sodium butyrate}}{C_3H_7.COONa} + NaOH \rightarrow \underset{\text{Propane}}{C_3H_8} + Na_2CO_3 .$$

(2) By the reduction of propyl iodide with zinc-copper couple and alcohol :

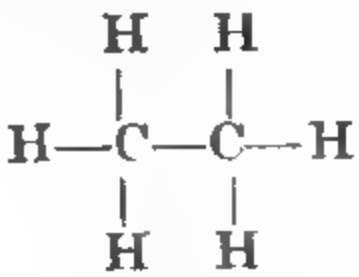
$$C_3H_7I + 2H \rightarrow C_3H_8 + HI$$

(3) By treating a mixture of methyl iodide and ethyl iodide with metallic sodium in ethereal solution (*Wurtz' reaction*).

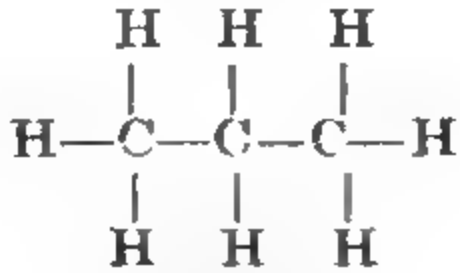
$$\begin{matrix} CH_3I \\ + \\ C_2H_5I \end{matrix} + 2Na \rightarrow C_3H_8 + 2NaI$$

Properties. Propane is a colourless gas, closely resembling ethane in its physical and chemical properties. It is stable towards acids, alkalies, oxidizing agents and reducing agents Like methane and ethane, propane yields *substitution products* with the halogens

Constitution. Propane is derived from ethane by the substitution of a hydrogen atom by a methyl group. The **structural relationship** of these two hydrocarbons will be evident from the following constitutional formulæ:



Ethane



Propane or
Methyl-ethane

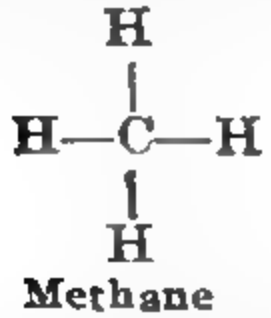
Derivatives. Propane gives rise to two series of mono-substitution products. Thus, with chlorine the following two **mono-chloropropanes** are produced :

(1) $CH_3.CH_2.CH_2.Cl$
1-Chloropropane
or *n*-Propyl chloride

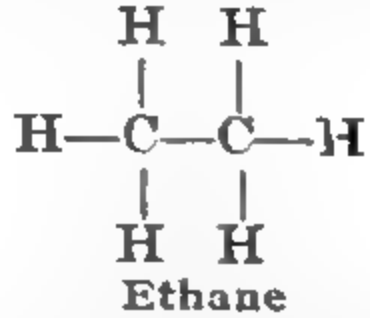
(2) $CH_3.CHCl.CH_3$
2-Chloropropane
or Isopropyl chloride

The compound (1) in which the chlorine atom has replaced one of the hydrogen atoms attached to a carbon atom at the *end* of the chain is called **normal propyl chloride or 1-chloropropane**. The compound (2) in which the chlorine atom has replaced the hydrogen from the *middle* carbon atom, is called **isopropyl chloride** or **2-chloropropane**.

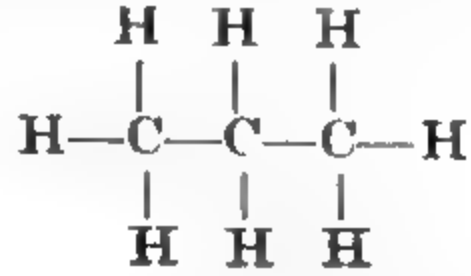
9. Isomerism. We are now in a position to understand the nature of the phenomenon of *isomerism*, and shall illustrate it with reference to *butanes*. It has been seen that ethane is derived from methane, and propane from ethane, by the substitution in each case, of a hydrogen atom by a methyl group. Since all the hydrogen atoms of methane, and also those ef ethane, are in a *similar* state of combination, there is only one ethane and only one propane possible.



Methane



Ethane



Propane

Now, the molecule of propane contains hydrogen in two *different* states of combination. Hence in this case. the replacement of hydrogen by the methyl group gives *two* different **butanes** having the same molecula formula, C_4H_{10} :

(1) $CH_3.CH_2.CH_2.CH_3$
n-Butane

(2) $CH_3.CH(CH_3).CH_3$
Isobutane

The first isomer, called normal butane or 1-methyl-propane is a straight chain compound, while the second, called isobutane, 2-methyl-propane, or trimethyl-methane, has a branched chain of carbon atoms. The two isomers are described in the following section.

10. Butanes, C_4H_{10}.

Preparation. ***n*-Butane** may be prepared by heating ethyl iodide with metallic sodium (Wurtz' reaction) :—

$$\underset{\text{Ethyl iodide}}{2CH_3.CH_2I} + 2Na \rightarrow \underset{\text{n-Butane}}{CH_3.CH_2.CH_2.CH_3} + 2NaI$$

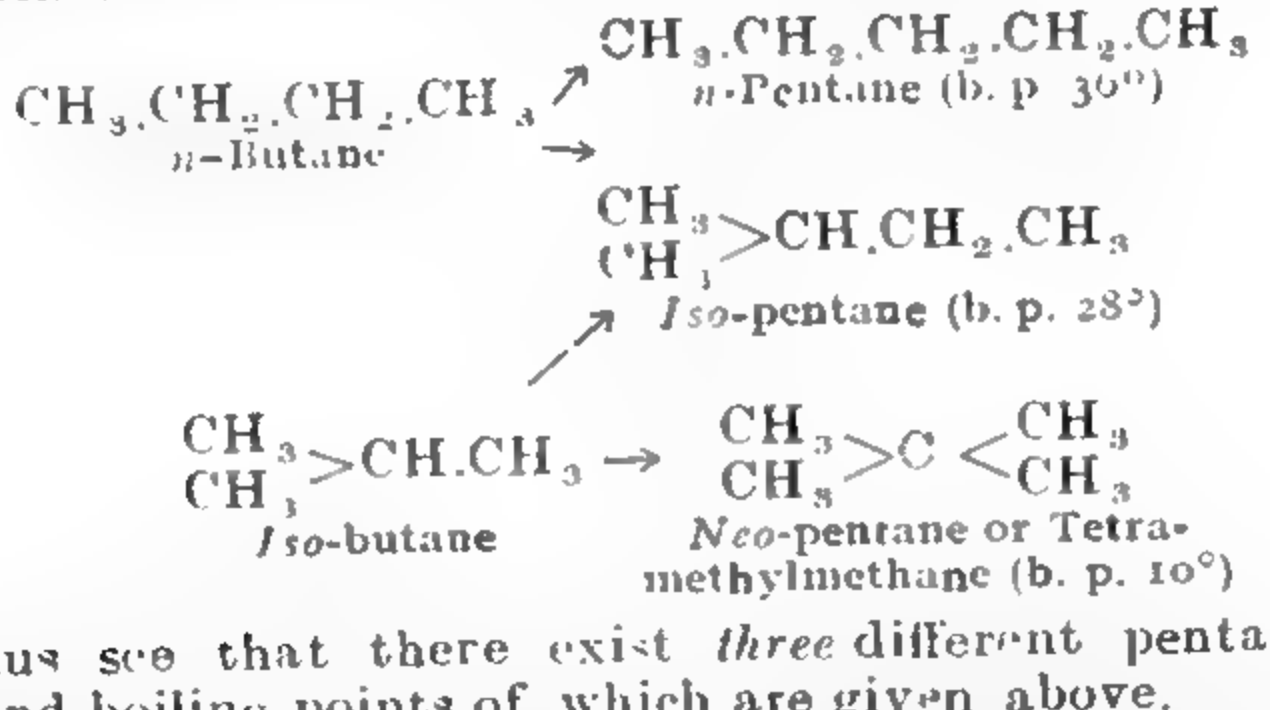
By using a mixture of isopropyl iodide and methyl iodide in this synthesis, **isobutane** is obtained :—

$$\underset{\text{Isopropyl iodide}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CHI} + 2Na + \underset{\text{Methyl iodide}}{ICH_3} \rightarrow \underset{\text{Isobutane}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_3} + 2NaI$$

The synthesis of the two butanes by Wurtz' reaction proves their respective structures.

Properties. Both the butanes are colourless gases at the ordinary temperature. Normal butane liquefies at + 1°, whereas isobutane can only be liquefied at − 17° under the atmospheric pressure. The isomers possess the usual chemical inertness towards acids, alkalies, oxidizing agents and reducing agents. They give substitution products with halogens.

11. Pentanes. The hydrogen atoms in the two butanes are in two different states of combination. Hence the replacement of hydrogen by methyl group, should, in each case, give rise to two different pentanes. Out of these four isomers, two are identical, as will appear from the following scheme :—



We thus see that there exist *three* different pentanes, the names, formulæ and boiling points of which are given above.

The three pentanes represent three different classes into which paraffin hydrocarbons are divided. They are designated as *normal*, *iso*-, and *neo*-paraffins respectively. The *normal* paraffins are straight-chain compounds, *i. e.* they contain no carbon atom in combination with more than two other carbon atoms. In an *iso*-paraffin there is at least one carbon atom in combination with three other carbon atoms, while in a *neo*-paraffin there is at least one carbon atom in combination with four others.

12. Alkyl Groups. We have seen that the *methyl* group is derived from methane by the removal of a hydrogen atom from the *methane* molecule. In the same manner, the homologues of methane gives rise to other monovalent alkyl groups. In the following table are given a few of the alkyl groups together with the names of the hydrocarbons

from which they are derived. It should be noted that the name of alkyl group is obtained from that of the corresponding paraffin hydrocarbon by replacement of the terminal *ane* by *yl*.

Hydrocarbons	Alkyl Group
Methane, CH_4	*Methyl group*, CH_3—
Ethane, C_2H_6	*Ethyl group*, C_2H_5—
Propane, $CH_3.CH_2.CH_3$	(*i*) *n-Propyl* group, $CH_3.CH_2.CH_2$–
	(*ii*) *Isopropyl* group, $(CH_3)_2CH$—

13. Composition of Gaseous Hydrocarbons. See Chapter 5, Sec. 8.

14. Natural Sources of Paraffins. The more important natural sources of paraffin hydrocarbons are :—

(1) **Petroleum** (see Sec. 15).

(2) **Natural Gas.** This is found usually in association with petroleum deposits. It contains about 85 per cent of methane, the rest being ethane and other hydrocarbons. It is extensively used in the United States and Canada as a fuel and illuminant and for raising steam in boilers.

(3) **Shale.** Bituminous shale, occurring in Scotland, France, and U.S.A. is an important source of liquid and solid paraffins. It is subjected to dry distillation, when ammonia, inflammable gases and shale tar are obtained. The latter, after being washed with concentrated sulphuric acid and caustic soda, is subjected to fractionation to obtain naptha, burning oil, lubricating oil and paraffin wax.

(4) **Brown Coal.** In Germany the most important natural source of paraffins is brown coal, from which naphtha, burning oil, lubricating oil and paraffin wax are obtained in the same way as described above for shale.

(5) **Ozokerite.** Ozokerite, or **earth wax,** is often found near the surface of the ground in certain localities. Extensive deposits occur in eastern Galicia. It is a dark-coloured material, consisting of solid paraffin hydrocarbons, and is supposed to have been formed by the evaporation of shallow deposits of petroleum. It is refined by melting out from earthy impurities, and the brownish product, after being treated with concentrated sulphuric acid and alkali, is decolorized with charcoal. The purified material is used as a substitute for beeswax under the name "**ceresin**".

15. Petroleum Industry. Petroleum is a thick, dark-coloured, oily liquid, consisting of a complex mixture of hydrocarbons. It occurs in enormous quantities below the surface of the earth in different parts of the world, notably in the United States, Mexico, Russia, Persia and Dutch East Indies.

Petroleum is brought to the surface by drilling wells through the overlying strata into the oil-bearing sand-stone. A section through an oil-field is shown in Fig. 5. If a boring be made in the middle, we would get only salt water. In the two positions where the wells are shown to be drilled we would get petroleum (right) and natural gas (left).

Crude petroleum is not generally refined at the oil-field but is sent

(*ii*) **Lubricating Oil.** The fractions that follow gas-oil are used as lubricating oils.

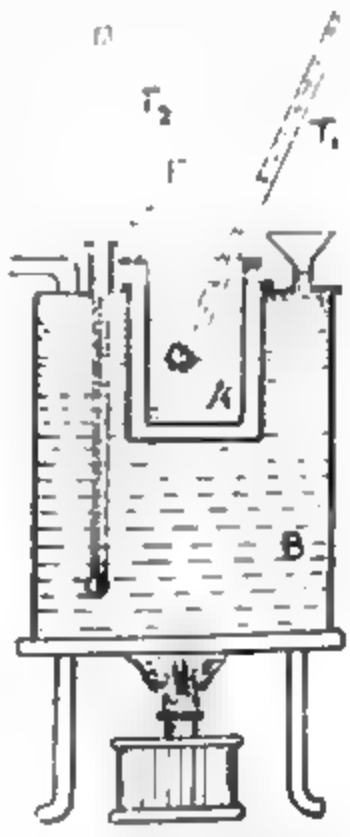
(*iii*) **Veseline.** This is the last fraction to pass, and is semi-solid in consistency. It is used in toilet, as a vehicle for ointments, and as a lubricant.

(4) **Tar.** The dark, tarry liquid that is left in the still is periodically drawn off, and is further distilled in cast-iron "coking" stills. The distillate consists of "heavy oil and paraffin" and is separated into *paraffin wax*, *lubricating oils*, and *eiseline* as described above. The residue in the stills is **Petroleum coke**, which is used as a household fuel.

(5) **Gas** The gas that comes off from the last condenser is subjected to pressure in order to separate the light gravity gasoline carried by it. The residual gas is burnt under the stills and in gas-engines. It is also used for making lampblack.

16. Flash Point Kerosene to be used in lamps should not be sufficiently volatile at ordinary temperatures to form explosive mixtures with air. The *lowest temperature at which an oil gives off a sufficient amount of vapour to form an explosive mixture with air* is termed its **flash point**. To protect the public against low-flash oils, which would be dangerous to use in lamps, laws have been made by different governments, forbidding the sale of oils having flash-points below a certain minimum. The minimum flash-point prescribed differs in different countries. In India, which has a hot climate, it is fixed at 44°C., while in France, which has a colder climate a minimum flash-point of 35 C, is permitted. In Great Britain, it is unduly low (22·1°C).

The flash-point of an oil is usualy determined by means of **Abel's apparatus** (Fig. 8). The sample to be tested is placed in a small metal cup, *A*, which is gradually heated by means of the surrounding water bath, *B*. A small test flame, *F*, is lowered into the space above the oil from time to time by means of an automatic device. As soon as the vapour ignites with a minute explosion, the temperature, indicated on the thermometer T_1 is noted. Besides this thermometer, which is graduated from 10° to 50° C., there is another, T_2, graduated from 50° to 75° C. for the water bath.



Abel's Flash-point Apparatus

Expt. 4 Place some kerosene oil in a beaker provided with a thermometer and heated on a water bath. After every one degree rise of temperature above 30°, test the vapour inside the beaker by means of a lighted match. The temperature at which the vapour ingnites with a small explosion is taken as the approximate flash-point of the oil.

QUESTIONS

1. How is methane prepared in the laboratory? What are the chief properties of this compound? "Methane is a saturated hydrocarbond." Explain this statement. *(Punjab, Inter. 1915)*

2. How will you prepare ethane from ethyl iodide? Draw a neat sketch of the apparatus.

3. Describe any three methods for the preparation of aliphatic saturated hydrocarbons. *(Punjab., Inter. 1943)*

4. Describe Wurtz' synthesis of the paraffin hydrocarbons. How, with the help of this reaction, may methane be converted into ethane?

5. Given some acetic acid, how will you proceed to prepare from it (*a*) methane, and (*b*) ethane?

thus obtained is known as **naphtha**. The geseous hydrocarbons (CH_4 to C_4H_{10}) that the crude oil contains in solution pass off uncondensed and may be collected in gas-holders.

The different products obtained in the above process are put to the following uses:—

(1) **Naphtha.** This is carefully refractionated, and separated into the following products :—

(*i*) **Petroleum ether** (C_4H_{10} to C_6H_{14}), which is employed as a solvent in the rubber and varnish industries.

(*ii*) **Petrol** or **gasoline** (C_6H_{14} to C_8H_{18}) which finds extensive application as a fuel in the motor and aeroplane engines. It is also used as a solvent, for dry cleaning, and for making petrol-air gas.

(*iii*) **Benzine.** This is used as a solvent, for dry cleaning and as a substitute for turpentine oil in the preparation of varnishes :

(2) **Kerosene Oil.** This is employed as an illuminant and a fuel.

(3) **Heavy Oil and Paraffin.** This fraction is strongly cooled to separate the solid constituents, which are used as **Paraffin wax.** The liquid portion, from which the wax has been separated, is redistilled in a current of steam, and separated into the following fractions :—

(*i*) **Fuel Oil** *or* **Gas Oil.** This is the first fraction, and is employed as fuel oil in Diesel engines. It is also used for making oil-gas and gasoline by a process of **craking,** *i. e.*, heating to a high temprature, whereby the higher hydrocarbons break up into the lower hydrocarbons —

$$C_{16}H_{34} \rightarrow 2C_4H_{12} + C_6H_{14} + 2C$$

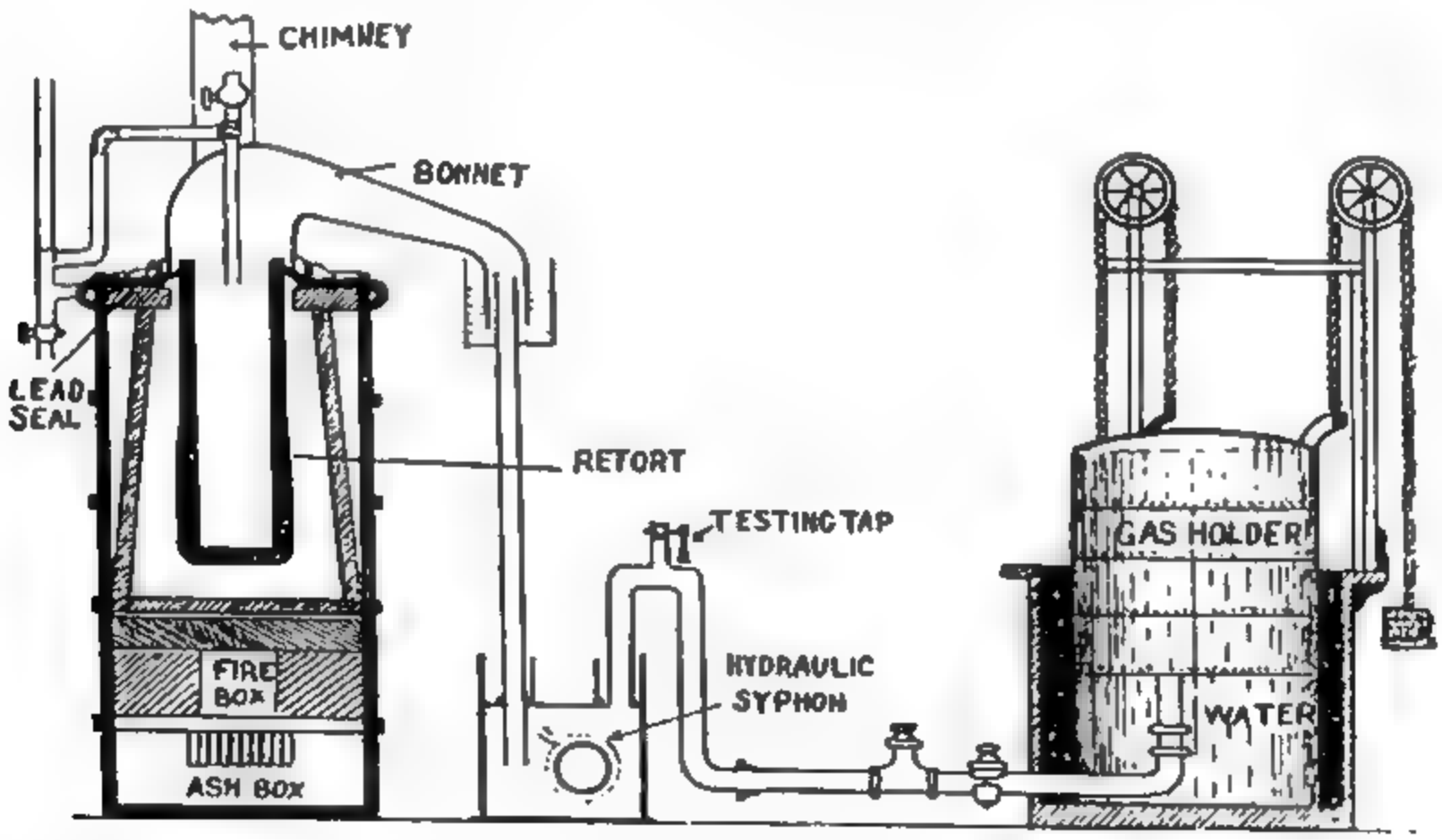


Fig. 7. Oil Gas Plant.

In making **oil-gass,** a thin stream of oil is allowed to flow into a cast-iron retort heated to dull redness (Fig, 7). The cracking of the liquid hydrocarbons occurs with production of gaseous hydrocarbons, methane, ethane, ethylene, etc. The gas is first passed through a scrubbing box, which retains the tarry matter present in it, and is then collected in gas-holders.

Large quantities of **cracked gasoline** are nowadays obtained by forcing the fuel oil through pipe coils set in a furnace, and fractionating the product

CHAPTER 8

UNSATURATED HYDROCARBONS

1. An unsaturated hydrocarbon is one in which the maximum combining capacity of one or more pairs of carbon atoms is not fully utilized. There are two chief homologous series of unsaturated aliphatic hydrocarbons, one represented by *ethylene*, C_2H_4, and the other by *acetylene*, C_2H_2.

2. Ethylene, *Ethene*, $H_2C{=}CH_2$.

Occurrence. Ethylene occurs to the extent of about 5 per cent in coal gas from the coking ovens. It is also present in wood-gas.

Preparation. (1) *From Ethyl Alcohol.* In the laboratory, ethylene is usually obtained by heating a mixture of ethyl alcohol and concentrated sulphuric acid to about 160°. The reaction has been shown to take place in two stages: First, ethyl hydrogen sulphate, $C_2H_5HSO_4$, is produced, which decomposes to give ethylene and sulphuric acid :

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5.HSO_4 + H_2O$$
$$C_2H_5.HSO_4 \rightleftharpoons C_2H_4 + H_2SO_4$$

Expt 1. A mixture of 30 ml of ethyl alcohol and 75 ml. of concentrated sulphuric acid and enough sand to form a thin paste is placed in a large size, round-bottom flask provided with a delivery tube and a dropping funnel (**Fig. 1**). The stem of the latter should be drawn out to a fine point and slightly bent so that it

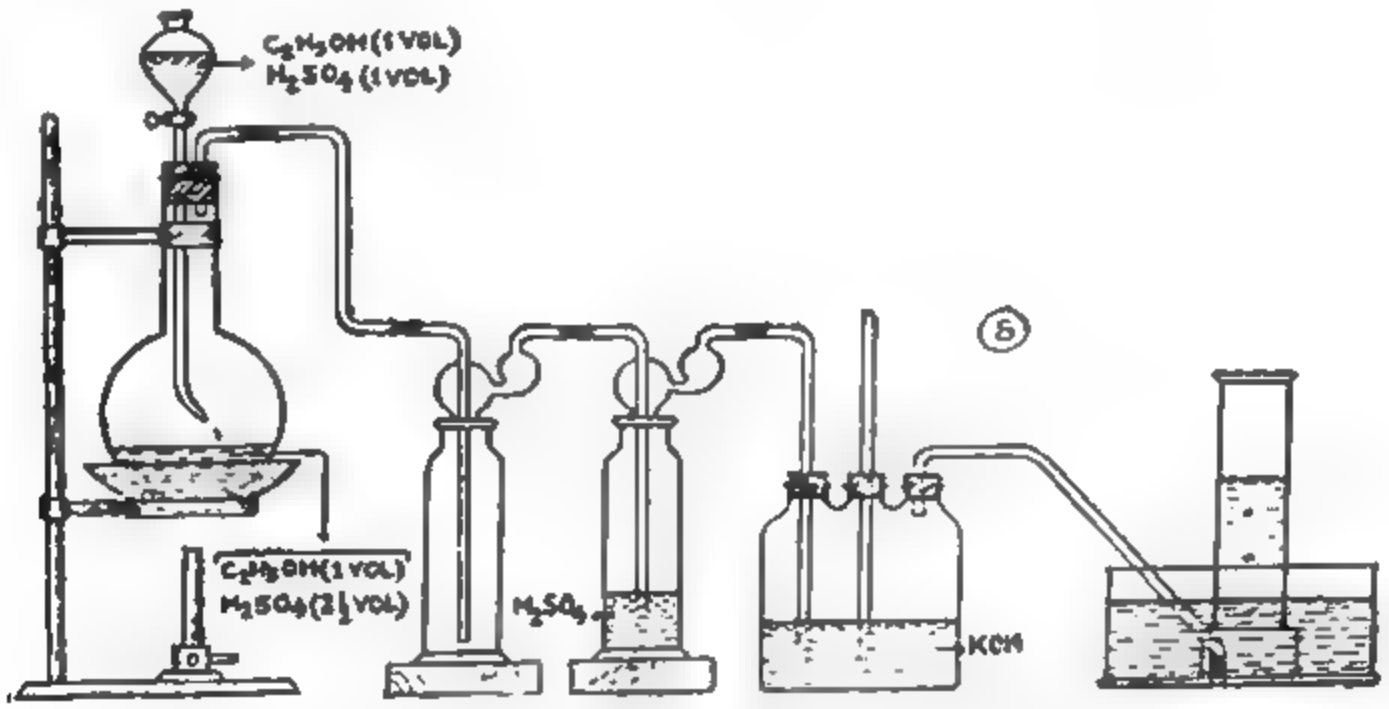


Fig. 1 Preparation of Ethylene.

could be kept filled with liquid and thus prevent the escape of the gas through it. The object of adding sand to the mixture in the flask is to prevent frothing. The flask is heated on a sand bath, until a steady stream of gas is evolved (160—165°C) When the evolution of gas becomes slow, a further supply may be obtained by dropping a mixture of equal volumes of alcohol and concentrated sulphuric acid. The evolved ethylene is contaminated with alcohol and ether vapours, carbon dioxide and sulphur dioxide. It is therefore passed first through a cold, empty wash-bottle, in order to condense alcohol and ether vapours, then through one or more wash-bottles containing a solution of potassium hydroxide, to remove carbon dioxide and sulphur dioxide. The gas thus purified is collected over water in gas cylinders.

An alternative method of preparing ethylene, free from carbon dioxide and sulphur dioxide, consists in dropping ethyl alcohol into syrupy phosphoric acid heated to about 220°C. As the reaction is continuous, an almost unlimited amount of the alcohol can be decomposed by a relatively small amount of phosphoric acid.

Expt. 2. About 50 ml. of syrupy phosphoric acid (sp. gr 1·75) are placed in a 250 ml. distillation flask provided with a dropping funnel (the stem of which is drawn to a fine point reaching to the bottom of the flask) and a thermometer (the bulb of which dips in the acid). The flask is heated on a sand bath, until the temperature rises to 220° and then a quantity of alcohol is run in very slowly. The evolved gas is passed through a wash-bottle surrounded by ice, in order to condense water, alcohol and ether vapours, and is then collected over water.

(2) *From Ethyl Bromide.* Ethylene may also be produced by heating ethyl bromide with an *alcoholic* solution of potassium hydroxide. The reaction involves the removal of a molecule of hydrogen bromide :—

$$\underset{\text{Ethyl bromide}}{CH_3.CH_2Br} + KOH \longrightarrow \underset{\text{Ethylene}}{H_2C{=}CH_2} + KBr + H_2O$$

(3) *From Succinic Acid.* Ethylene is also produced when a concentrated, aqueous solution of potassium succinate is submitted to electrolysis (anodic oxidation of anion) :—

$$\underset{\text{Potassium Succinate}}{\begin{matrix} H_2C.COOK \\ | \\ H_2C.COOK \end{matrix}} \rightleftharpoons \begin{matrix} H_2C.COO^- \\ | \\ H_2C.COO^- \end{matrix} + 2K+$$

$$\begin{matrix} H_2C.COO^- \\ | \\ H_2C.COO^- \end{matrix} \longrightarrow \begin{matrix} H_2C \\ \| \\ H_2C \end{matrix} + 2CO_2 + 2e^-$$

The reaction is analogous to that used in the preparation of ethane from an alkali acetate (Chap.7, Sec. 3).

Manufacture. Ethylene is prepared on a large scale by three different methods :—

(1) By passing alcohol vapour through a heated tower filled with coke moistened with syrupy phosphoric acid.

(2) By passing alcohol vapour through heated tubes containing kaolin (china clay) or alumina (Al_2O_3).

(3) In the natural gas region, by *cracking* ethane by passing it through heated tubes,

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Physical Properties. Ethylene is a colourless gas, having a faint, ethereal odour. It is sparingly soluble in water, but fairly so in alcohol and ether.

Chemical Properties. (1) *Combustion.* Ethylene burns with a luminous flame, and, like other hydrocarbons, forms an explosive mixture with air or oxygen :

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

(2) *Combination with Hydrogen.* In the presence of finely-divided nickel, ethylene combines with hydrogen yielding ethane :

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + H_2 \rightarrow \underset{\text{Ethane}}{H_3C.CH_3}$$

This reaction and the reactions that follow are termed **addititon reactions.** They involve the *conversion of a double bond into a single bond.* Addition reactions are characteristic of ethylene and other unsaturatd compounds, and distinguish them from saturated hydrocarbons and their derivatives, which **react only** by *substitution.* The compounds obtained by the direct addition of an unsaturated compound with

other substances are called **addition compounds**, or **additive compounds**; while those produced from a saturated compound by substitution are known as **substitution products.**

The addition of hydrogen to an unsaturated compound in the presence of finely-divided nickel is known as **hydrogenation.** It is of great commercial importance, for with its help liquid oils (which, like ethylene, are *unsaturated*) are converted into solid fats (which are *saturated*). The manufacture of **artificial ghee** is based on this reaction.

(3) *Combination with Halogens.* Ethylene combines directly with chlorine, bromine and iodine, yielding dihalogen addition products ; *e g.*,

$$\underset{\text{Ethylene}}{\overset{CH_2}{\overset{\|}{CH_2}}} + Br_2 \rightarrow \underset{\text{Ethylene bromide}}{\overset{CH_2Br}{\overset{|}{CH_2Br}}}$$

The decolorization of bromine water is characteristic of all unsaturated compounds, and is employed as a test for **unsaturation.**

(4) *Combination with Halogen Hydrides.* Ethylene combines readily with hydrogen iodide, and less readily with hydrogen bromide, yielding alkyl halides :

$$\underset{\text{Ethylene}}{H_2C=CH_2} + HI \rightarrow \underset{\text{Ethyl iodide}}{CH_3.CH_2I}$$

(5) *Combination with Hypochlorous Acid.* Ethylene combines with hypochlorous acid, in dilute aqueous solution, yielding a **cholorohydrin**:—

$$H_2C=CH_2 + HOCl \rightarrow \underset{\text{Ethylene chlorohydrin}}{CH_2Cl.CH_2OH}$$

(6) *Combination with Sulphuric Acid.* Ethylene is readily absorbed by concentrated sulphuric acid with the formation of ethyl hydrogen sulphate :

$$H_2C=CH_2 + H.HSO_4 \rightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3.CH_2.HSO_4}$$

If the resulting liquid containing ethyl hydrogen sulphate be heated, ethylene is set free :

$$C_2H_5.HSO_4 \rightarrow C_2H_4 + H_2SO_4$$

The absorption of ethylene by concentrated sulphuric acid may, therefore, be employed for the **removal** or **separation of ethylene from a mixture of gases.**

Another use of this reaction is in the **conversion of ethylene into ethyl alcohol.** This is brought about by diluting the liquid containing ethyl hydrogen sulphate with water and boiling :

$$\underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{C_2H_5.HSO_4} + H\,OH \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4$$

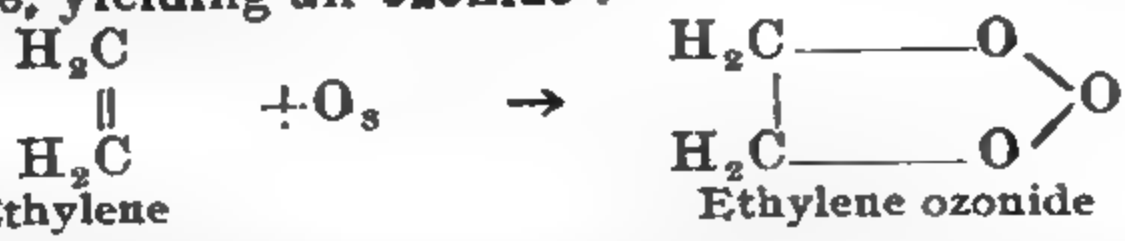
It is thus possible to effect the indirect addition of the elements of water to ethylene.

(7) *Reaction with Permanganate:* When ethylene is treated with a cold, dilute alkaline solution of potassium permanganate (**Baeyer's reagent**), it yields a dihydric alcohol, called **ethylene glycol** :

$$\underset{\text{Ethylene}}{\overset{CH_2}{\overset{\|}{CH_2}}} + H_2O + O \rightarrow \underset{\text{Ethylene glycol}}{\overset{CH_2OH}{\overset{|}{CH_2OH}}}$$

The decolorization of **Baeyer's reagent** in the cold constitutes **another delicate test for unsaturation.**

(8) *Combination with Ozone.* Ethylene combines directly with a molecule of ozone, yielding an **ozonide** :



Ethylene — Ethylene ozonide

Expt. 3. (*a*) Ignite a cylinder of ethylene. Notice that it burns with a bright flame.

(*b*) Invert a jar containing ethylene over another containing chlorine. Notice that the colour of chlorine soon disappears with the simultaneous production of oily drops of ethylene chloride.

(*c*) Repeat the above experiment, using bromine vapour instead of chlorine.

(*d*) Pour some bromine water into a jar of ethylene, and shake. Notice that the colour of bromine disappears.

(*e*) Repeat the above experiment with a dilute, alkaline solution of potassium permanganate. Notice the decolorization.

Uses. (1) Ethylene is now being used instead of acetylene for *cutting* and *welding*. Though inferior to acetylene as far as the flame temperature goes, it has a distinct advantage over the latter in that it can be stored and transported in cylinders under high pressure without danger of explosion.

(2) It is also finding an extensive use in the fruit industry. Fruit is gathered and transported before it is fully ripe. On its arrival, it is kept for a few days in an atmosphere containing a small proportion of ethylene, which rapidly develops the colour and completes the ripening process.

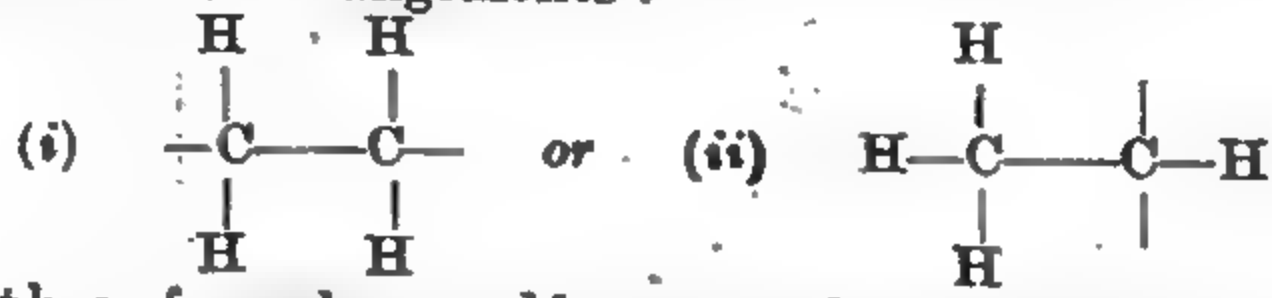
(3) In recent years, ethylene has come into large use as an anaesthetic in place of ether

(4) Large quantities of ethylene are used in the preparation of *ethylene glycol*, *ethylene chlorohydrin*, *ethylene chloride* and during war time, of *mustard gas*.

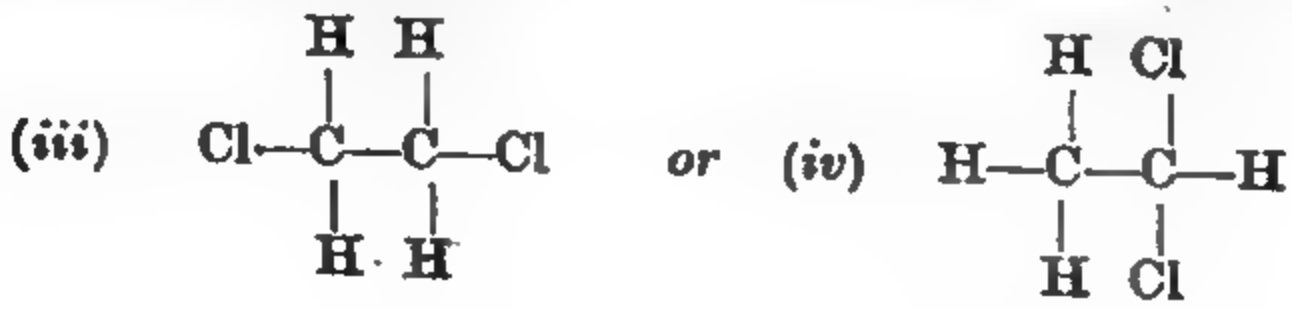
3. Constitution of Ethylene. The constitution of ethylene is based on the following considerations :

(1) The molecular formula of the hydrocarbon, as determined by the method described in Chapter 5, Section 8, is C_2H_4.

(2) As in the case of ethane, the two carbon atoms must be *directly* linked together. Hence, the ethylene molecule may have one of the following two atomic arrangements :



Each of these formulae would account for the addition of two monovalent atoms or groups to the molecule. Thus the addition of chlorine will give a product (ethylene chloride), which would possess one of the following constitutions :—



(3) When acetaldehyde, a compound which has been shown to possess the structural formula $CH_3.CHO$, is treated with phosphorus pentachloride, its oxygen atom is replaced by two chlorine atoms. The resulting compound, called ethylidene chloride, must, therefore, possess the structure $CH_3.CHCl_2$, *i.e.*, formula (*iv*) given above. Hence, ethylene chloride (which is isomeric with ethylidene chloride, but possesses different properties) must be given the alternative structure (*iii*). The ethylene molecule must therefore, have the atomic arrangement (*i*) and not (*ii*).

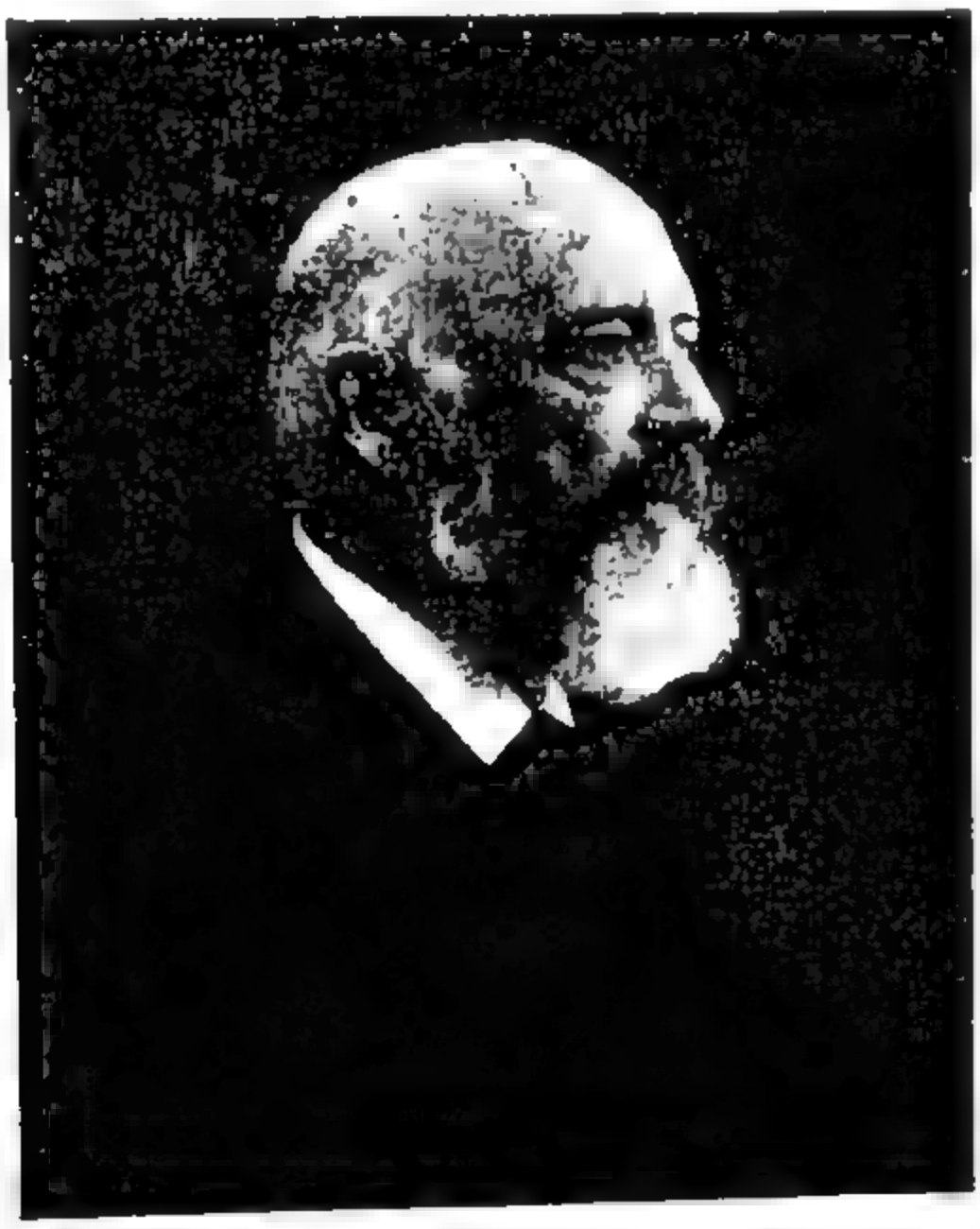
(4) Now, formula (*i*) shows ethylene to possess "free" or unsatisfied valencies—a condition that appears to be impossible as shown by the facts given below :—

(*a*) The failure of all attempts to isolate alkyl radicals such as $—CH_3$, $—C_2H_5$, etc.

(*b*) The impossibility of isolating methylene, CH_2 (the hypothetical first member of the ethylene series), in which the two unsatisfied valencies must necessarily be associated with one carbon atom.

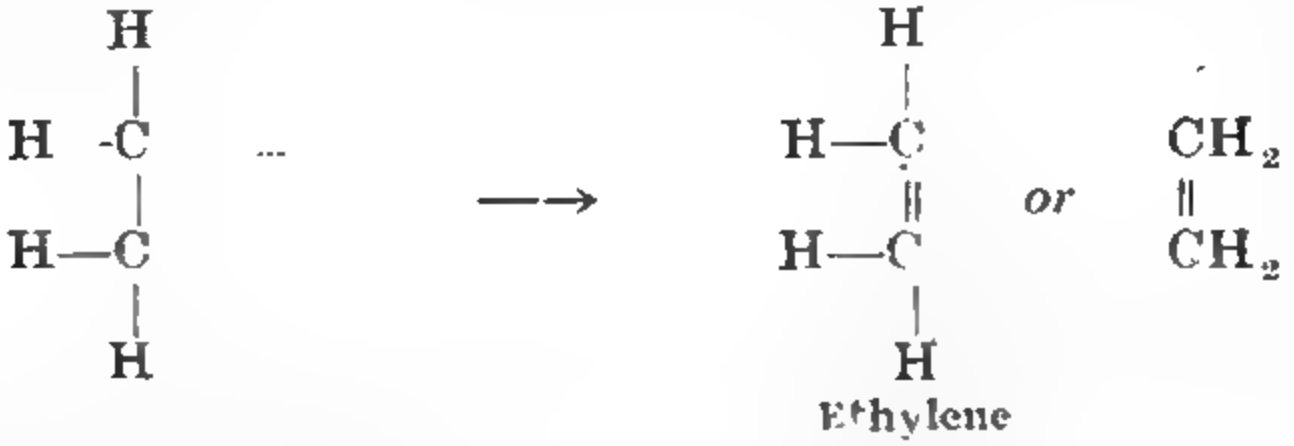
(*c*) In formula (*i*) there are *two* "free valencies". It might be expected that they could be satisfied *one at a time*, by the addition of halogens, and a compound of the formula $XCH_2—CH_2—$ would, in that case, be possible. Actually, however, two halogen atoms are always added *simultaneously* with the formation of a completely saturated compound.

For the reasons given above, it is supposed that in ethylene the two unsatisfied valencies of the carbon atoms satisfy each other, thus



JOHNN FRIEDRICH WILHELM ADOLF VON BAEYER
(1835—1917).
German chemist, who is well-known as the founder of the Strain Theory.

giving rise to what is known as a **double bond, ethylene linkage, or an ethenoid linkage :**



Ethylene

It is important to remember that the double bond in ethylene, as in any other unsaturated compound, is the point at which the molecule shows the maximum reactivity. This interesting fact is explained by Baeyer by means of his strain theory

It has been shown by Le Bel and van't Hoff that the four valency bonds of the carbon atom are directed towards the angular points of a regular tetrahedron, at the centre of which the carbon atom is supposed to lie. Baeyer pointed out that when two atoms get bound together by means of a double bond, the valencies concerned in the formation of the double bond must undergo a bending or distortion from their normal positions. A strain is thus set up in the molecule, which renders the double bond easily attackable by reagents. The tension thus produced in the molecule may be conveniently represented by a pair of flexible wires (*see* Fig. 2).

The **mechanism of addition reactions** that an unsaturated compound readily undergoes may be beautifully illustrated by means of atomic models, as in Fig. 2. The combination of ethylene (*A*) with bromine is here represented as being preceded by the *rupture* of the double bond, as shown at *B*. The product of the reaction is dibromoethane (*C*) which is a saturated compound having normally directed valencies.

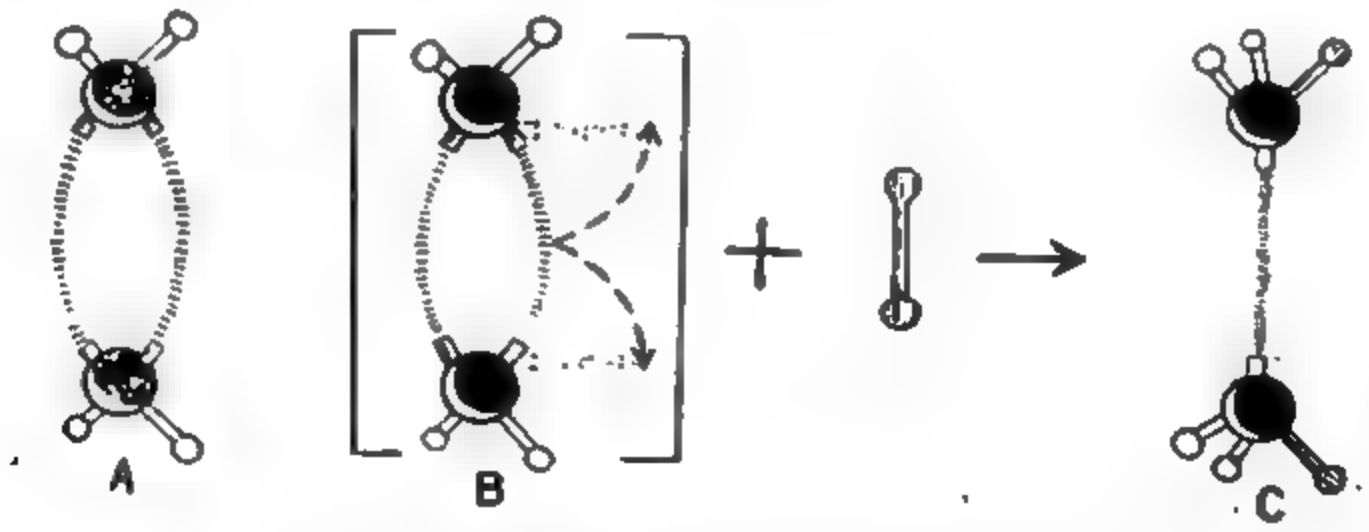
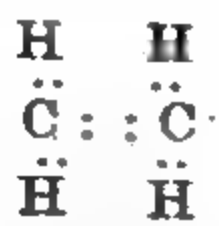


Fig. 2. Atomic Model Representation of the Combination of Ethylene with Bromine.

Electronic Formula. The electronic formula of ethylene is as under :



The two carbon atoms are held together by a double covalent bond, in the formation of which each of the carbon atoms has contributed a pair of electrons. The four hydrogen atoms are linked to the carbon

atoms by single covalent bonds, as in methane and ethane molecules.

4. Homologues of Ethylene. Ethylene is the first member of a homologous series of unsaturated hydrocarbons, called the **olefines**. The general formula of this series is C_nH_{2n}. The names of various olefines are derived from the corresponding saturated hydrocarbons by changing the terminal *-ane* to *-ylene* or *-ene*. A few of the simple olefines are :—

Ethylene, or *ethene*, $H_2C{=}CH_2$
Propylene, *propene*, or methyl-ethylene, $H_2C{=}CH.CH_3$
Butylenes, or *butenes*, C_4H_8

Olefines, like paraffins, exhibit isomerism. Thus, there are as many as three butylenes ; *viz* ,

(1) Ethyl-ethylene, $H_2C{=}CH.CH_2.CH_3$
(2) Symmetrical dimethyl-ethylene, $CH_3.CH{=}CH.CH_3$
(3) Unsymmetrical dimethyl-ethylene, $H_2C{=}C(CH_3)_2$.

5. General Methods of Preparation. The olefines are prepared by the following methods :—

(1) *By the dehydration of alcohols.* This is effected by heating the alcohols with concentrated sulphuric acid, phosphoric acid, or zinc choloride; *e.g.*,

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \rightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O$$

$$\underset{n\text{-Propyl alcohol}}{CH_3.CH_2.CH_2OH} \rightarrow \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + H_2O$$

(2) *By the removal of a molecule of halogen hydride from an Alkyl Halide.* This is effected by boiling the alkyl halide with *alcoholic* potash; *e.g.*,

$$\underset{\text{Ethyl bromide}}{CH_3.CH_2Br} + KOH \rightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2} + KBr + H_2O$$

$$\underset{\text{Propyl bromide}}{CH_3.CH_2.CH_2Br} + KOH \rightarrow \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + KBr + H_2O$$

(3) *By the electrolysis of concentrated solutions of potassium salt of dibasic acids of the succinic series, e.g.,*

$$\underset{\text{Potassium succinate}}{\begin{matrix}H_2C.COOK\\|\\H_2C.COOK\end{matrix}} + \begin{matrix}HOH\\HOH\end{matrix} \rightarrow \underset{\text{Ethylene}}{\begin{matrix}H_2C\\\|\\H_2C\end{matrix}} + 2CO_2 + 2KOH + H_2$$

$$\underset{\begin{matrix}\text{Potassium salt of}\\\text{dimethylsuccinic acid}\end{matrix}}{\begin{matrix}CH_3.CH.COOK\\|\\CH_3.CH.COOK\end{matrix}} + \begin{matrix}HOH\\HOH\end{matrix} \rightarrow \underset{\begin{matrix}\text{s-Dimethyl}\\\text{ethylene}\end{matrix}}{\begin{matrix}CH_3.CH\\\|\\CH_3.CH\end{matrix}} + 2CO_2 + 2KOH + H_2$$

In this reaction, a mixture of the olefine hydrocarbon and carbon dioxide is evolved at the anode, while hydrogen and potassium hydroxide are produced at the cathode.

6. General Properties. As in other homologous series, the members of this series show a gradual change in physical properties with the increase in carbon atoms. The lower members, up to C_4H_8, are gases, the following fourteen or so are liquids, while the higher ones are solids. Olefines, like other hydrocarbons, are readily soluble in alcohol or benzene and practically insoluble in water.

All the olefines contain a double bond in their molecule, and give additive compounds with hydrogen, halogens, halogen hydrides, sulphuric acid, ozone, etc., in exactly the same manner as ethylene.

7. Acetylene, *Ethine*, HC ≡ CH.

Occurrence. Acetylene occurs in coal gas to the extent of about 0·06 per cent. When a Bunsen burner strikes back, the gases formed contain up to 0·8 percent. of acetylene.

Synthesis. Acetylene was first synthesized by Berthelot in 1859 by sparking carbon electrodes in a current of hydrogen (Fig. 3)

$$2C + H_2 \rightarrow C_2H_2.$$

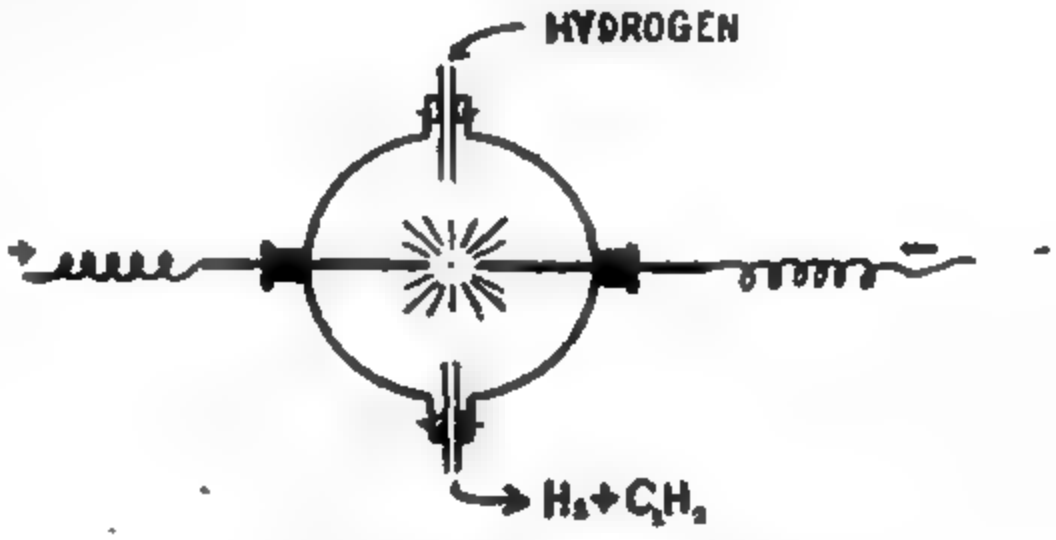


Fig. 3. Synthesis of Acetylene from Carbon and Hydrogen.

Preparation. (1) ***From Calcium Carbide.*** Acetylene is most readily prepared by dropping water on calcium carbide:

$$Ca\begin{matrix}C\\ \|\\ C\end{matrix} + 2H.OH \rightarrow Ca(OH)_2 + \begin{matrix}CH\\ \|\\ CH\end{matrix}$$

Calcium carbide — Acetylene

The gas evolved from the commercial carbide is contaminated with ammonia, hydrogen sulphide and phosphine. It may be washed with an *acid* solution of cupric sulphate, which removes the above impurities.

Expt. 45. Fit up the apparatus shown in Fig. 4. Place a layer of sand in the filtering flask, and cover this with a few pieces of calcium carbide. Place a solution of cupric sulphate, acidified with hydrochloric acid, in the gas washing bottle. Admit water slowly through the dropping funnel, and collect the evolved gas over water.

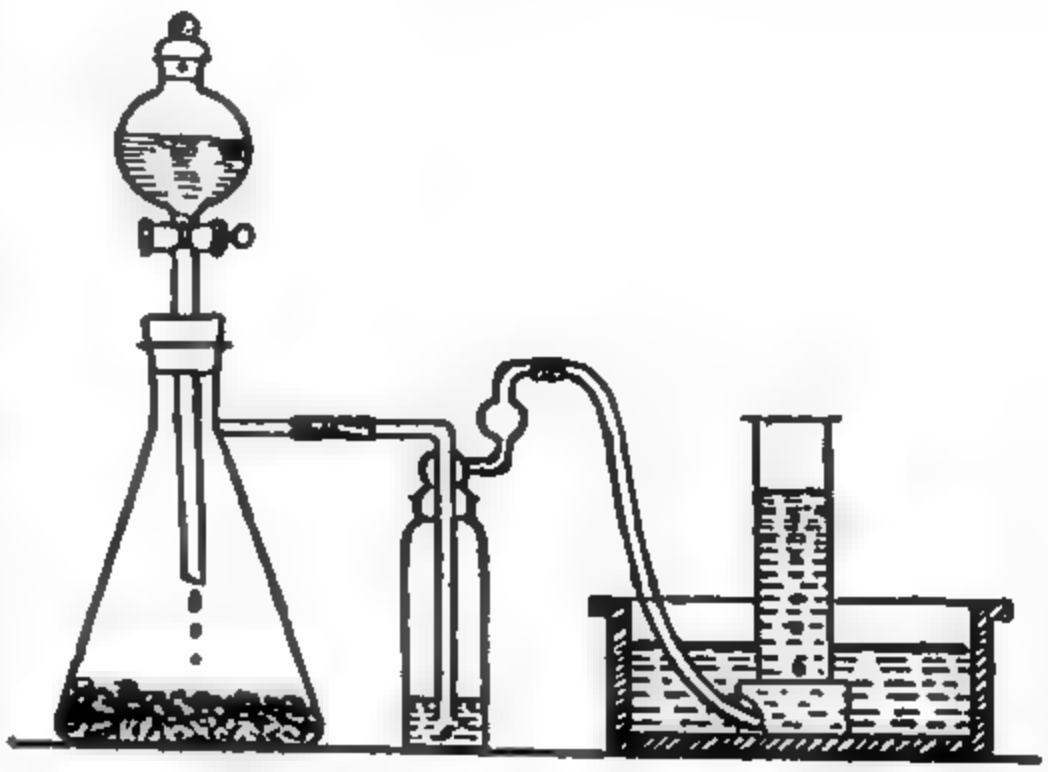


Fig. 4. Preparation of Acetylene from Calcium Carbide.

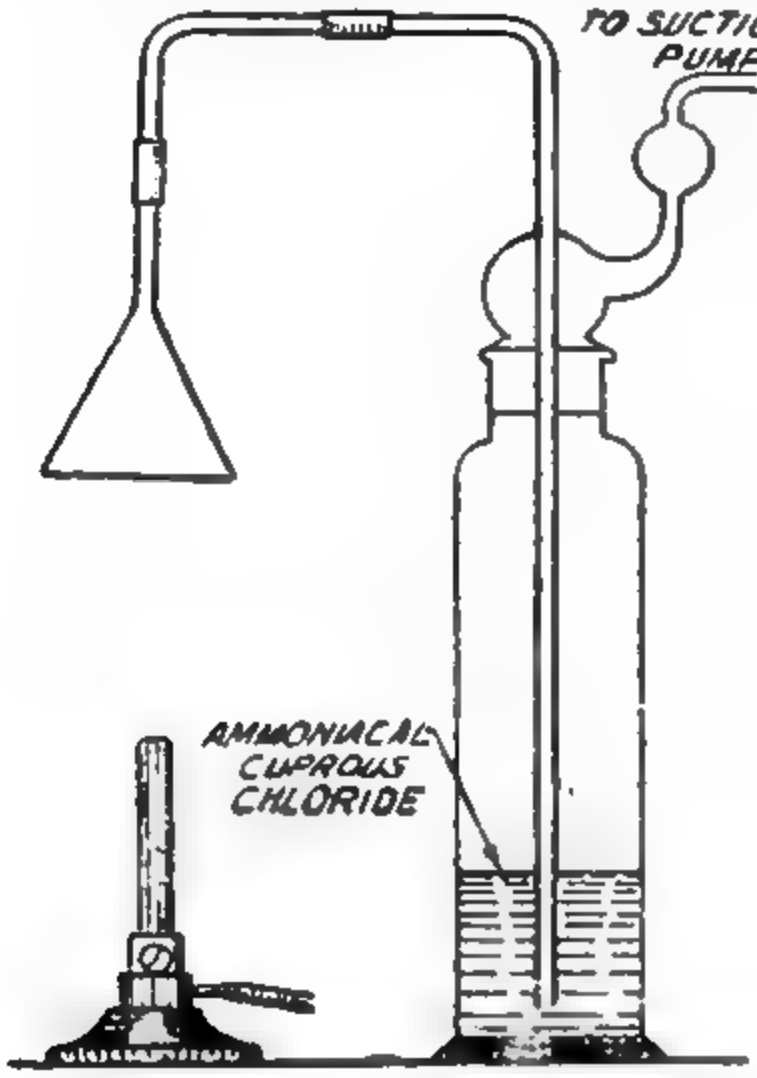
(2) ***From Ethylene Bromide.*** When ethylene bromide, $C_2H_4Br_2$, is heated with alcoholic potash, it loses two molecules of hydrogen bromide, yielding acetylene (compare formation of ethylene from ethyl bromide, *p.* 65) :—

$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + 2KOH \rightarrow \begin{matrix}CH\\ \|\\ CH\end{matrix} + 2KBr + 2H_2O$$

Ethylene bromide — Acetylene

(3) The formation of acetylene during incomplete combustion of coal gas or ether may be shown by means of the following experiments.

Expt. 5. Light a Bunsen burner at the base, and aspirate the resulting gases through a Drechsel bottle containing some ammoniacal cuprous chloride solution (Fig. 5). It will be observed that a reddish-brown precipitate of cuprous acetylide is formed.



Fsg 5.

Expt. 6. Pour some ammoniacal solution of cuprous chloride into a wide boiling-tube, and then add a little ether. Light the ether at the mouth of the tube, and, while it is burning, hold the tube in a slanting position and give it a slow rotatory motion. It will be observed that a precipitate of cuprous acetylide is formed in this case also.

(4) Acetylene is also formed when a solution of the sodium or potassium salt of fumaric or maleic acid is submitted to electrolysis, (anodic oxidation of the anion) ;—

$$\begin{array}{l} CH\,COOK \\ \| \\ CH.COOK \end{array} \rightleftharpoons \begin{array}{l} CH.COO^- \\ \| \\ CH.COO^- \end{array} + 2K+$$

$$\begin{array}{l} CH.COO^- \\ | \\ CH.COO^- \end{array} \longrightarrow \begin{array}{l} CH \\ \| \\ CH \end{array} + 2CO_2 + 2e-$$

This reaction is analogous to that used in the preparation of ethane from an alkali acetate (Chapt. 7, Sec. 3)

Physical Properties Acetylene is a colourless gas, which, when pure, has a peculiar ethereal smell. The objectionable odour of the gas prepared from the commercial carbide is due to impurities, especially phosphine. Water dissolves about 1 volume alcohol 6 volumes, and acetone 25 volumes of the gas under the ordinary conditions.

Caution Acetylene cannot be safely stored under a pressure greater than 2 atmospheres, as it is then liable to explode violently by mere shock. In storing acetylene, advantage is sometimes taken of the fact that acetone can dissolve 300 volumes of the gas under a pressure of 12 atmospheres. It is in the form of acetone solutions (which, unlike gaseous acetylene, are not liable to explode) that acetylene is transported in steel cylinder, when required for welding, cutting steel, etc.

Chemical Properties. (1) Acetylene is an unstable compound. When submitted to a pressure of more than 2 atmospheres and detonated, it decomposes into its elements with explosive violence :

$$C_2H_2 \rightarrow 2C + H_2$$

For industrial purposes, the gas is stored by forcing it into cylinders packed with briquettes soaked in acetone, which absorb 300 vols. of the gas at 15° and under 12 atmospheres pressure.

(2) Acetylene burns with a luminous, smoky flame. When burnt from a jet with a very fine aperture, the flame is not smoky but exceedingly luminous. In an acetylene burner, the gas issues from two small openings so arranged that the two fine streams of gas strike against each other to produce a flat flame. Side-holes are provided, through which air is sucked in and gets mixed with the gas as it rushes through the nozzle. The result is a flame that is non-smoky and highly luminous. Acetylene is used for this reason in cycle lamps and for illuminating

houses, etc , where electric supply is not available.

The oxy-acetylene blow-pipe (Fig. 7) gives the hottest of all flames (temp. = 2700°C), and is used for welding, cutting and making holes in steel plates

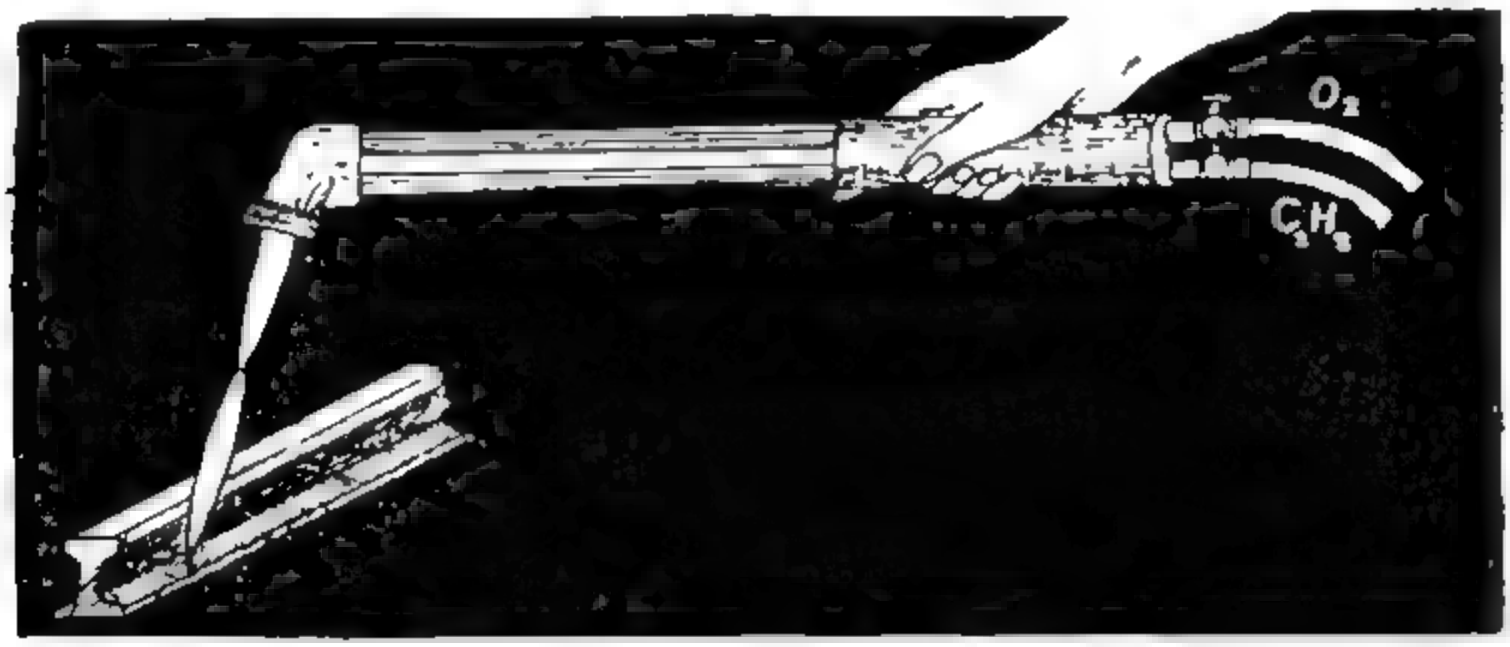


Fig. 7. Oxy-acetylene Torch

Like all hydrocarbons, acetylene forms an explosive mixture with air.

Expt. 7. (*a*) Light some acetylene contained in a gas-cylinder Notice that it burns with a very smoky flame

(*b*) Light the gas in an acetylene burner. Notice that the flame is of dazzling brilliancy.

(3) ***Addition Reactions.*** Acetylene, like ethylene, is an unsaturated compound, and since it contains a triple bond, *i. e. four* unsaturated valencies, it combines with four monovalent atoms or groups, the reaction taking place in *two steps* as in the following cases :—

(*i*) *Combination with Hydrogen* :

$$\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow{+H_2} \underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow{+H_2} \underset{\text{Ethane}}{CH_3.CH_3}$$

(*ii*) *Combination with Halogens* :—

$$\underset{\text{Acetylene}}{\begin{matrix}CH\\\|\\CH\end{matrix}} \xrightarrow{+Br_2} \underset{\text{Acetylene dibromide}}{\begin{matrix}CHBr\\\|\\CHBr\end{matrix}} \xrightarrow{+Br_2} \underset{\text{Acetylene tetrabromide}}{CHBr_2.CHBr_2}$$

(*iii*) *Combination with Halogen Hydrides* :

$$\underset{\text{Acetylene}}{\begin{matrix}CH\\\|\\CH\end{matrix}} \xrightarrow{+HBr} \underset{\text{Vinyl bromide}}{\begin{matrix}CH_2\\\|\\CHBr\end{matrix}} \xrightarrow{+HBr} \underset{\text{Ethylidene bromide}}{\begin{matrix}CH_3\\|\\CHBr_2\end{matrix}}$$

It should be noted that in the second stage of the reaction the halogen atom goes to that carbon atom which carries the *smaller* number of hydrogen atoms **(Markownikoff's rule)**

(*iv*) *Combination with Sulphuric Acid.* Like ethylene, acetylene is absorbed by sulphuric acid :—

$$\begin{matrix}CH\\\|\\CH\end{matrix} + 2H_2SO_4 \rightarrow \underset{\text{Ethylidene hydrogen sulphate}}{CH_3.CH(HSO_4)_2}$$

When the solution is diluted with water, and then distilled, acetalde-

hyde passes over :—

$$CH_3.CH(HSO_4)_2 + H_2O \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO} + 2H_2SO_4$$

The net result of the reaction, therefore, is the addition of a molecule of water (compare conversion of ethylene into ethyl alcohol, *p.* 66) :—

$$HC \quad CH + H_2O \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

(*c*) *Addition of Water.* A more direct method of adding the elements of water to acetylene consists in passing the gas into warm, 20 per cent sulphuric acid containing a little mercuric sulphate (catalyst) :

$$HC{-}CH + H_2O \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

This reaction is of great commerical importance and is employed in the **manufacture of acetaldehyde**

(4) **Polymerization.** When acetylene is heated at a dull red heat, it undergoes polymerization, yeilding benzene, C_6H_6.

$$\underset{\substack{\text{Acetylene}\\(3\text{ molecules})}}{3HC{\equiv}CH} \rightarrow \underset{\text{Benzene}}{\begin{matrix} & CH & \\ HC & & CH \\ HC & & CH \\ & CH & \end{matrix}}$$

The reaction is of great theoretical importance, since it affords a **method of passing from the aliphatic to the aromatic series.**

Note. The term *polymerization* refers to a chemical reaction involving the direct union of two or more molecules of a substance to form a new compound, whose molecular weight is a multiple of that of the original substance.

(5) **Formation of Metallic Derivatives.** When acetylene is passed through an ammoniacal solution of silver nitrate, it produces a white precipitate of silver acetylide, C_2Ag_2 :

$$C_2H_2 + 2AgNO_3 \rightarrow C_2Ag_2 + 2HNO_3$$
$$HNO_3 + NH_4OH \rightarrow NH_4NO_3 + H_2O \qquad [\times 2]$$
$$C_2H_2 + 2AgNO_3 + 2NH_4OH \rightarrow C_2Ag_2 + 2NH_4NO_3 + 2H_2O$$

Similarly, with an ammoniacal solution of cuprous chloride a brownish-red precipitate of **cuprous acetylide,** C_2Cu_2, is produced.

The formation of these precipitates is employed as **a distinctive test** for acetylene, and serves to distinguish it from the hydrocarbons of the ethylene and of the methane series. Further, since the acetylides are decomposed by acids with regenration of acetylene, their formation is also utilized for the **separation** of acetylene from a mixture of hydrocarbons.

$$C_2Cu_2 + 2HCl \rightarrow C_2H_2 + 2CuCl$$

Expt. 8. (*a*) Place a cylinder containing acetylene over another containing chlorine. Notice that the mixture ignites *spontaneously* with the deposition of carbon and formation of fumes of hydrogen chloride.

(*b*) Throw a small piece of calcium carbide into a trough containing water and bring the end of the delivery tube of a chlorine generator near the bubbles of acetylene as they rise from water. Notice that the bubbles of the gas ignite spontaneously.

(*c*) Pour some ammoniacal silver nitrate solution into a cylinder full of acetylene. Notice that a white precipitate of silver acetylide is formed.

(*d*) Pour some ammoniacal cuprous chloride solution into another cylinder of acetylene. Notice the formation of a reddish-brown precipitate of cuprous acetylide.

Uses. (1) As already mentioned, acetylene is used as an illuminant and in the oxy-acetylene torch.

(2) Acetylene is a *synthetic agent* of great importance. It can be readily obtained from its elements, and is very reactive. These two facts make acetylene almost indispensable in a large number of "complete syntheses" of organic substances. The advent of cheap electric energy, derived mainly from water-power, has made it possible to produce calcium carbide, and therefore, acetylene, very cheaply. Hence, the possibility of utilizing acetylene for the manufacture of organic substances of economic value has recently attracted much attention.

The most important **synthetic uses** of acetylene are :

(1) Conversion of acetylene into *acetaldehyde* (*p.* 74), which in turn yields:—

(*i*) *Ethyl alcohol*, by reduction : $CH_3CHO + H_2 \rightarrow CH_3.CH_2OH$,

(*ii*) *Acetic acid*, by oxidation : $CH_3CHO + O \rightarrow CH_3COOH$,

(*iii*) *Ethyl acetate*, by polymerization in the presence of aluminium ethoxide (catalyst) :

$$2CH_3CHO \rightarrow CH_3COOC_2H_5$$

In addition to the above three compounds, a number of other important aliphatic compounds of simple constitution have been obtained from acetylene *via* acetaldehyde. More complex substances, such as *artificial rubber*, have also been obtained by this means.

(2) Conversion of acetylene into *benzene* at a dull red heat (*p.* 89) may some day prove to be of great commercial importance, though so far it cannot be said to possess any practical significance

(3) Combination of acetylene with chlorine yields acetylene tetrachloride, $C_2H_2Cl_4$, which is used extensively as a solvent under the name of **westron.**

Constitution. The molecular formula of acetyeene, as determined by the method explained in Sec. 8, Chap. 5 is C_2H_2. Its constitution follows from its formation from ethylene bromide (*p.* 71), the two carbon atoms being linked together by a **triple bond.** This view is fully supported by the chemical behaviour of the hydrocarbon. The representation of the acetylene molecule by atomic models is shown in Fig. 8.

Fig. 8. Atomic Representation of Acetylene.

Electronic Formula. The electronic formula of acetylene is :—

$$H : C : : : C : H$$

The two carbon atoms are held together by a **triple covalent bond,** in the formation of which the carbon atoms have contributed *three* electrons each. The two hydrogen atoms are linked to the carbon atom by single covalent bonds as in ethane and ethylene.

8. Homologues of Acetylene. Acetylene hydrocarbons constitute a homologous series having the **general molecular formula** C_nH_{2n-2}. The following are the first four members of this series :

Acetylene, or *ethine*, $HC \equiv CH$
Propine, or methyl-acetylene, $HC \equiv C.CH_3$
Butine-1, or ethyl-acetylene $HC \equiv C.CH_2.CH_3$
Butine-2, or dimethyl-acetylene, $CH_3.C \equiv C.CH_3$

General Methods of Preparation. The following general methods are employed for the preparation of acetylene hydrocarbons :

(1) *By the removal of two molecules of halogen hydride from the dihalogen addition products of olefines.* This is effected, as usual, by heating the halogen compound with alcoholic potash.

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \\ \text{Ethylene bromide} \end{matrix} + 2KOH \rightarrow \begin{matrix} CH \\ \| \\ CH \\ \text{Acetylene} \end{matrix} + 2KBr + 2H_2O$$

$$\begin{matrix} CH_3CHBr \\ | \\ CH_2Br \\ \text{Propylene bromide} \end{matrix} + 2KOH \rightarrow \begin{matrix} CH_3.C \\ \| \\ CH \\ \text{Propine} \end{matrix} + 2KBr + 2H_2O$$

Since the olefines can be readily converted into dibromides, this reaction affords an easy method for the **conversion of olefines into acetylenes**.

$$\begin{matrix} CH_2 \\ | \\ CH_2 \\ \text{Ethylene} \end{matrix} \xrightarrow{+Br_2} \begin{matrix} CH_2Br \\ | \\ CH_2Br \\ \text{Ethylene bromide} \end{matrix} \xrightarrow[\text{KOH}]{\text{Alcoholic}} \begin{matrix} CH \\ \| \\ CH \\ \text{Acetylene} \end{matrix}$$

(2) *From aldehydes and ketones by successive treatment with phosphorus pentachloride and alcoholic potash* :

$$\begin{matrix} CH_3.CHO \\ \text{Acetaldehyde} \end{matrix} \xrightarrow{PCl_5} \begin{matrix} CH_3.CHCl_2 \\ \text{Unsymmetrical dichloroethane} \end{matrix} \xrightarrow{-2HCl} HC \equiv CH \quad \text{Acetylene}$$

$$\begin{matrix} CH_3.CO.CH_3 \\ \text{Acetone} \end{matrix} \xrightarrow{PCl_5} \begin{matrix} CH_3\,CCl_2.CH_3 \\ \text{2 : 2-Dichloropropane} \end{matrix} \xrightarrow{-2HCl} \begin{matrix} CH_3C \equiv CH \\ \text{Propine} \end{matrix}$$

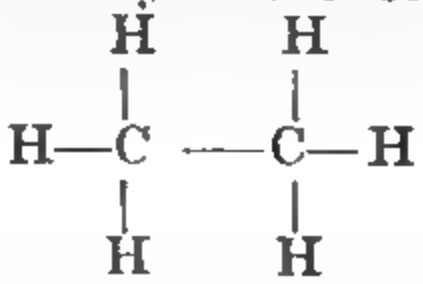
(3) *From complex organic substances by dry distillation.* The presence of acetylene in coal gas is due to this cause.

General Properties. Acetylene hydrocarbons up to $C_{14}H_{26}$ are gases, or volatile liquids, with a peculiar odour. The higher homologues are solids Like other hydrocarbons, acetylenes are insoluble in water and soluble in alcohol, benzene and petroleum ether

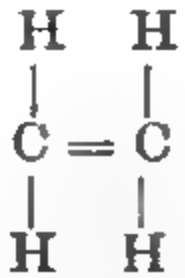
In chemical behaviour, the acetylene hydrocarbons closely resemble acetylene itself, except that the *members having no hydrogen in direct union with a triply-linked carbon atom* (*e.g.*, dimethyl-acetylene, $CH_3.C \equiv C.CH_3$) *do not yield metallic derivatives.*

Structural Relationship of Ethane, Ethylene and Acetylene, and their Interconversion. If each of the two carbon atoms of the ethane molecule be imagined to lose an atom of hydrogen, there will be left a pair of unsatisfied valencies. These will no sooner come into existence than satisfy each other, producing a *double bond*, the compound thus obtained being ethylene. It is, therefore, evident that *ethylene is a derivative of ethane* containing two atoms of hydrogen

less than the latter hydrocarbon.



Ethane



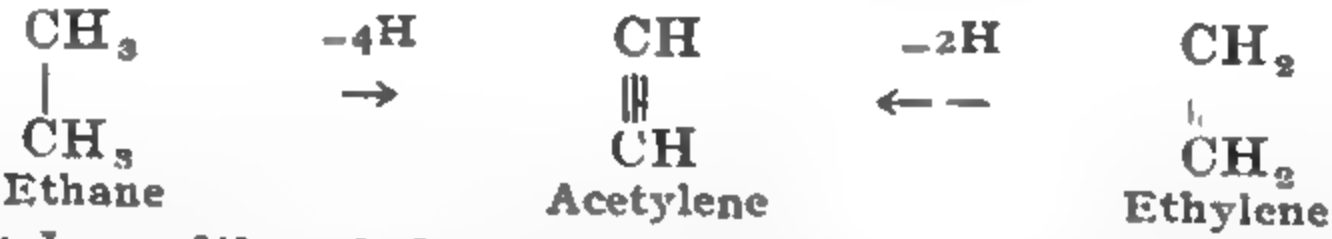
Ethylene

The relationship of ethane and ethylene is fully supported by their conversion into each other. We have seen that ethylene may be converted into ethane by *hydrogenation*.

$$H_2C{=}CH_2 + H_2 \rightarrow H_3C{.}CH_3$$

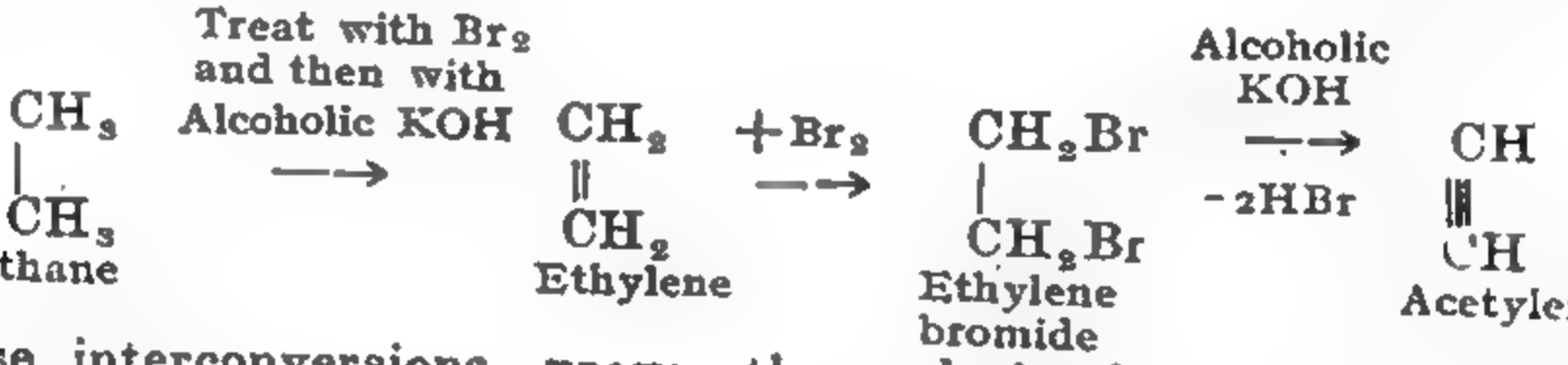
Conversely, ethane may be converted into ethylene by the following series of reactions :—

If the ethane molecule be supposed to lose *two* pairs of hydrogen atoms (or the ethylene molecule *one* pair) between the two carbon atoms, a *triple bond* will come into existence with production of acetylene :—



Hence, *acetylene, like ethylene, is a derivative of ethane* containing four atoms of hydrogen less than the parent hydrocarbon.

Acetylene may be converted into ethane by hydrogenation, while reverse change can be effected through the following series of reactions :—



These interconversions prove the relationship existing between ethane and acetylene.

10. Methane, the Parent Hydrocarbon of the Aliphatic Series. We have already seen that ethane is a derivative of methane (chap. 7, Sec. 5). Ethylene and acetylene have in the above section been shown to be derived from ethane. Hence, they are also derivatives of methane. In the same manner, *all* the compounds that we have to study in part II of this book can be shown to have been derived from methane. Hence, methane is the parent hydrocarbon of the aliphatic series.

11. Interconversion of Methane and Ethane (*Ascent and Descent of Series*). Methane can be converted into ethane through the following series of reactions :—

This is an example of passing up a homologous series, *i.e.*, synthesizing a higher homologue from a lower homologue.

The reverse change, *i e.*, passing down the series, can be brought about through the reactions shown below :—

CH_3 (Ethane) —Bromination→ CH_2Br (Ethylene bromide) —Alcoholic KOH→ $CH \equiv CH$ (Acetylene) —Treat with 20% H_2SO_4 in presence of $HgSO_4$→

$CH_3.CHO$ (Acetaldehyde) —Oxidation→ CH_3COOH (Acetic acid) —Heat sodium salt with soda-lime→ CH_4 (Methane)

QUESTIONS

1. Describe the preparation and properties of ethylene and acetylene, and show how they can be distinguished from each other. Write their full graphical formulae. (*Ajmer, Inter.*, 1931)

2. What do you understand by Unsaturation in organic compounds ? What reactions are characteristic of this state ? (*Punjab, Inter.*, 1917, 1920)

3. Give two methods for the preparation of ethylene and contrast the general properties of ethylene with those of ethane. (*Unit. Prov, Inter.*, 1928)

4. How would you prepare ethylene from ethyl alcohol ? Draw a sketch of the apparatus you would use, and mention the important properties of ethylene. How can it be distinguished from ethane ? Give equations. (*Unit Prov., Inter.*, 1934)

5. Give the methods of preparation, physical and chemical properties, and uses of acetylene. (*Ajmer Inter.*, 1934)

6. Compare the properties of ethylene and acetylene. How are they prepared ? (*Unit. Prov., Inter., 1923*)

7. How would you separate and identify the components of a mixture of methane, ethylene, acetylene and carbon dioxide ? Explain fully the chemistry of the process you employ. (*Punjab, Inter., 1927*)

8. Explain the meaning of the following terms : (*a*) Additive product. (*b*) Double bond ; (*c*) Triple bond ; (*d*) Polymerization.

9. 10 ml. of a hydrocarbon and 45 ml. of oxygen were enclosed in a eudiometer over mercury and exploded. After explosion and cooling, the volume of gases was reduced to 35 ml. On addition of caustic soda, there was further reduction to 15 ml. What is the composition of the hydrocarbon ? (*Ans.* C_2H_4). (*Punjab, Inter., 1922*)

10. How may the following conversions be effected ? :—
   (*i*) Ethane into ethylene ;
   (*ii*) Ethylene into ethane ;
   (*iii*) Ethylene into acetylene
   (*iv*) Acetylene into ethylene.

11. How will you convert ethylene into the following compounds ?
   (*i*) Ethylene chlorohydrin ;
   (*ii*) Ethyl alcohol ;
   (*iii*) Formaldehyde ;
   (*iv*) Ethylene glycol.

12. Describe the reaction by which acetylene may be converted into :—
   (*i*) Ethylidene bromide ;
   (*ii*) Acetaldehyde ;
   (*iii*) Benzene ;
   (*iv*) Cuprous acetylide.

13. Discuss the structural relationship of ethane, ethylene and acetylene ? Why are all these compounds regarded as derivatives of methane ?

14. Explain the terms *ascent* and *descent of homologous series*. Illustrate these by reference to methane and ethane.

CHAPTER 9

HALOGEN DERIVATIVES OF HYDROCARBONS

1. The halogen derivatives of the aliphatic hydrocarbons provide the most valuable starting material for the synthesis of aliphatic compounds, and, for this reason, are dealt with before any other class of derivatives.

HALOGEN DERIVATIVES OF PARAFFINS

2. Monohalogen Derivatives. These are derived from the paraffin hydrocarbons by the replacement of only one hydrogen atom by a halogen atom. They may also be regarded as *esters* of the halogen acids, and, for this reason, they are more commonly called **alkyl halides**.

3. Formation of Alkyl Halides. Alkyl halides are obtained by the following general methods :—

(1) From *paraffins*, by the action of halogens in the presence of sunlight ; *e.g.*,

$$CH_4 + Cl_2 \rightarrow \underset{\text{Chloromethane (methyl chloride)}}{CH_3Cl} + HCl$$

The reaction, however, is *not* suitable fer preparing alkyl halides, as it proceeds further to give mixtures of isomerides and higher halogen derivatives.

(2) From *olefines*, by the direct combination with halogen hydracids ; *e.g.*,

$$C_2H_4 + HI \rightarrow \underset{\text{Ethyl iodide}}{C_2H_5I}$$

(3) From *alcohols*, by the action of halogen acids or phosphorus halides :

$$(i)\ \underset{\text{Methyl alcohol}}{CH_3OH} + HCl \rightleftharpoons \underset{\text{Methyl chloride}}{CH_3Cl} + H_2O$$

$$(ii)\ \underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \rightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

Reaction (*i*) is reversible; and some means to eliminate water must be adopted. In **Grove's process** for preparing alkyl chlorides, the alcohol, to which some anhydrous zinc chloride has been added, is saturated with gaseous hydrogen chloride. Another method consists in distilling a mixture of alcohol, sodium halide and concentrated sulphuric acid.

When preparing alkyl bromides and iodides by reaction (*ii*) it is not necessary to employ previously prepared phosphorus halides : the halogen is gradually added to a mixture of alcohol and phosphorus, and the whole is then warmed to complete the reaction.

(4) From *alkyl sulphates*, by the action of a metallic halide in aqueous solution :

$$\underset{\text{Methyl suplhate}}{(CH_3)_2SO_4} + KI \rightarrow \underset{\text{Methyl iodide}}{CH_3I} + CH_3.KSO_4$$

4. Physical Properties of Alkyl Halides. Only a few of the alkyl halides, *viz.* CH_3Cl, C_2H_5Cl, and CH_3Br, are gases under ordinary conditions. The majority are colourless, pleasant-smelling liquids. Like other esters, alkyl halides are practically insoluable in water, but readily dissolve in alcohol, ether, carbon disulphide, and other organic solvents.

5. Chemical Properties of Alkyl Halides :—

(*a*) ***Non-polar Character.*** Alkyl halides differ characteristically from the metalic halides. As is well known, the latter compounds react instantaneously with aqueous silver nitrate, yielding a precipitate of silver halide. Alkyl halides, on the other hand, being non-electrolytes, either do not react with silver nitrate or the reaction proceeds very slowly.

(*b*) ***Substitution Reactions.*** It must not be concluded from (*a*) that the halogen in alkyl halides is particularly firmly bound. As a matter of fact, the aliphatic halogen compounds are among the most reactive of all organic compounds. The halogen atom is easily removed and replaced by other atoms or groups. This property renders them of great importance in synthetic organic chemistry, as is illustrated by the following reactions :—

(1) When an alkyl halide is treated with zinc-copper couple and alcohol or tin and hydrochloric acid, the halogen atom is replaced by *hydrogen* with the production of the corresponding paraffin ; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \rightarrow \underset{\text{Ethane}}{C_2H_6} + HI$$

(2) When heated with aqueous potash, the halogen atom is replaced by the *hydroxyl* group, with the production of an alcohol; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KOH \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KI$$

The conversion of an alkyl halide into an alcohol is an example of **hydrolysis**. The term is applied to a *reaction involving a double decomposition between water, H.OH, and another substance the reaction taking place in such a way that the hydroxyl group of water goes to the electropositive part of the other molecule and the hydrogen atom to the electronegative part.*

In the hydrolysis of an alkyl halide by aqueous alkalies, the *primary* reaction is hydrolysis :—

$$C_2H_5I + H.OH \rightleftharpoons C_2H_5OH + HI$$

The alkali present simply serves to neutralize the halogen hydride produced in the reaction,

$$HI + KOH \rightarrow KI + H_2O$$

and thus enables the reversible reaction between the alkyl halide and water to proceed to completion.

(3) When an alkyl halide is heated with sodium or zinc, the halogen atom of one molecule gets replaced by the *alkyl* group of the other, with the production of a higher paraffin (**Wurtz' Synthesis**) ; *e.g.*,

$$\underset{\text{Ethyl iodide}}{2C_2H_5I} + Zn \rightarrow \underset{n\text{-Butane}}{C_2H_5.C_2H_5} + ZnI_2$$

(4) When an alkyl halide is heated with a sodium derivative of an alcohol, the halogen atom is replaced by an *alkoxyl* group, with the production of an ether ; *e.g.*,

$$C_2H_5I + NaOCH_3 \rightarrow \underset{\text{Mathyl ethyl ether}}{C_2H_5.O.CH_3} + NaI$$

(5) Similarly, with the silver salt of a carboxylic acid, the halogen atom gets replaced by an *acyloxyl* group with the production of an ester *e.g.*,

$$\underset{\text{Silver acetate}}{CH_3COOAg} + C_2H_5I \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgI$$

(6) When heated with an alcoholic solution of ammonia in a sealed tube, the halogen atom is replaced by an *amino group*, with the production of an amine ; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + NH_3 \rightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + HI$$

(7) When heated with potassium cyanide, the halogen atom is replaced by the *cyano group*, with the production of an alkyl cyanide : *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KCN \rightarrow \underset{\text{Ethyl cyanide}}{C_2H_5CN} + KI$$

This reaction is of great importance, as the alkyl cyanides are easily converted into *carboxylic acids* by hydrolysis with mineral acids or alkalies :—

$$C_2H_5CN + 2H_2O \rightarrow \underset{\text{Propionic acid}}{C_2H_5COOH} + NH_3$$

The conversion of an alkyl halide into alkyl cyanide involves the introduction of an additional atom of carbon into the molecule. Hence, it affords a means of **ascending a homologous series**. Thus, methyl alcohol (a derivative of methane) may be converted into acetic acid (a derivative of ethane) by the following series of reactions :—

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{HI} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{H.OH} \underset{\text{Acetic acid}}{CH_3COOH}$$

(8) When heated with silver nitrite, the halogen atom is replaced by the *nitro group*, with the production of a nitro-paraffin ; *e.g.*,

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + AgNO_2 \rightarrow \underset{\text{Nitro-ethane}}{C_2H_5NO_2} + AgI$$

(*c*) ***Other Reactions***. The many-sided reactivity of alkyl halides and their use in synthetic organic chemistry is further shown by the following reactions that they undergo :—

(1) *Conversion into Olefine Hydrocarbons.* See Chap. 8, Sec. 4.

(2) **Grignard's Reaction.** When a dry ethereal solution of an alkyl halide is treated with dry magnesium, a magnesium alkyl halide is produced ; *e.g.*,

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + Mg \rightarrow \underset{\text{Magnesium ethyl bromide}}{C_2H_5.Mg.Br.}$$

This reaction, first discovered by Grignard, a French chemist, is of great practical importance. The resulting compounds, called **Grignard's reagents** are much used in the preparation of a large variety of organic substances.

(3) *Combination with Tertiary Amines.* Alkyl halides undergo direct addition with tertiary amines, forming quaternary ammonium salts ; *e.g.*,

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3I \rightarrow \underset{\text{Tetramethylammonium iodide}}{(CH_3)_4NI}$$

Individual Members.. A few of the alkyl halides in common use are given below. They all show the chemical properties given in the preceding section.

5. Methyl Chloride, or *Chloromethane*, CH_3Cl, is prepared by Grove's process : Methyl alcohol to which about half its weight of zinc chloride has been added, is saturated with hydrogen chloride. The mixture is then gently warmed over a water-bath, when methyl chloride passes over.

$$CH_3OH + HCl \rightleftharpoons CH_3Cl + H_2O$$

VICTOR GRIGNARD (1871—1935)

Professor of Chemistry at the University of Lyon, France. He was awarded the Nobel Prize for his discovery of the reaction, Alkyl Halides which have proved of great value in the synthesis of a large number of organic compounds.

Methyl chloride is a colourless, sweet-smelling gas which, on being cooled under pressure, condenses to a liquid boiling at −23°. Rapid evaporation of the liquid causes an intense heat absorption. The gas burns with a green-edged flame.

Uses. Methyl chloride is placed on the market in the liquid form. It is largely employed

(1) As a methyleting agent[1] in the manufacture of dyes, and

(2) For the production of low temperatures

6. Ethyl Chloride, C_2H_5Cl. Ethyl chloride or **chloro-ethane** is prepared by **Grove's process**. Absolute alcohol, to which about half its weight of anhydrous zinc chloride has been added, is saturated with hydrogen chloride in flask fitted with a reflux condenser and a safety tube (Fig. 1).

[1] *i.e.* for introducing methyl group into a molecule.

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + H_2O.$$

When the absorption of hydrogen chloride is complete the flask is gently heated on a water-bath. The alcohol vapour is mostly condensed in the reflux condenser, and the liquid flows back into the flask. From the top of the condenser the vapours are conducted into a flask containing water (the inlet tube being here cut off just above the surface of the liquid to prevent the back suction), and thence into a soda-lime

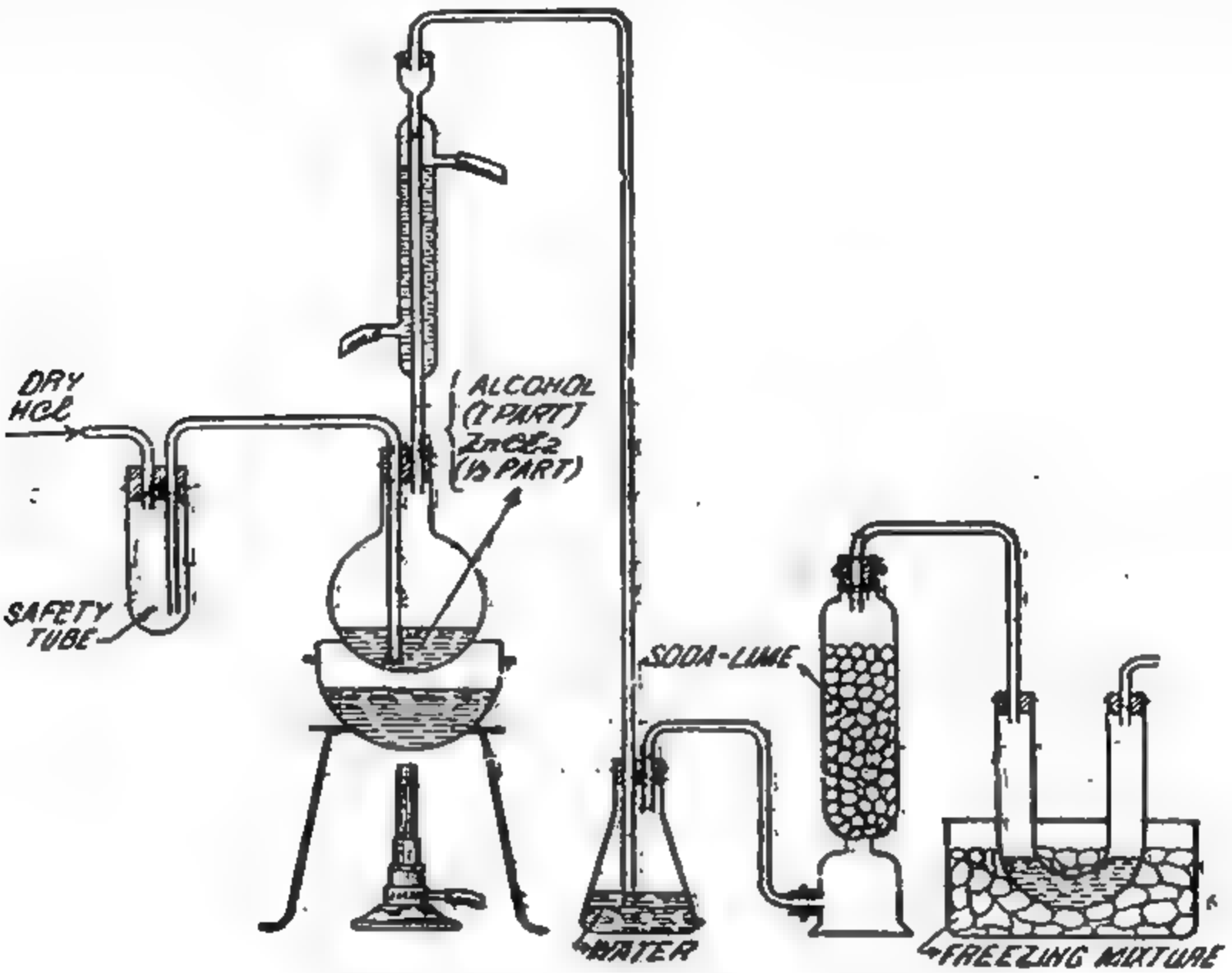


Fig. 1 Preparation of Ethyl Chloride.

tower. These serve to remove alcohol vapour, hydrogen chloride and moisture. The pure, dry ethyl chloride is then condensed in a U-tube immersed in a freezing-mixture.

Properties. Ethyl chloride is a colourless, sweet-smelling liquid boiling at 12°. The rapid evaporation of the liquid causes intense heat absorption. For this reason, it is used as a local anaesthetic.

Use. On account of the property just described (*i.e.*, of heat absorption) ethyl chloride is employed as a local anaesthetic.

7. Ethyl Bromide, C_2H_5Br, is readily obtained by distilling a mixture of potassium bromide, ethyl alcohol, and concentrated sulphuric acid.

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$
$$C_2H_5OH + HBr \rightleftharpoons C_2H_5Br + H_2O$$

Expt. 1. place 30 ml. of concentrated sulphuric acid in a distillation flask, add gradually 30 ml. of alcohol with constant shaking and cooling. Then add 30 gm. of coarsely powdered potassium bromide. Connect the flask to a Liebig condenser, and the latter to an adapter dipping under icecold water in a flask (Fig. 2) Heat the flask on a sand bath. Ethyl bromide passes over, and collects as a heavy, oily layer at bottom of the water in the receiver.

Separate the oil by means of a tap funnel, wash it first with its own volume of water, then with dilute sodium carbonate solution, and finally with water. Allow the

oil to stand over granular calcium chloride, until it becomes clear. Then decant it into a distillation flask, and redistil. Collect the fraction passing over at 37°—40°, and seal it in a glass tube.

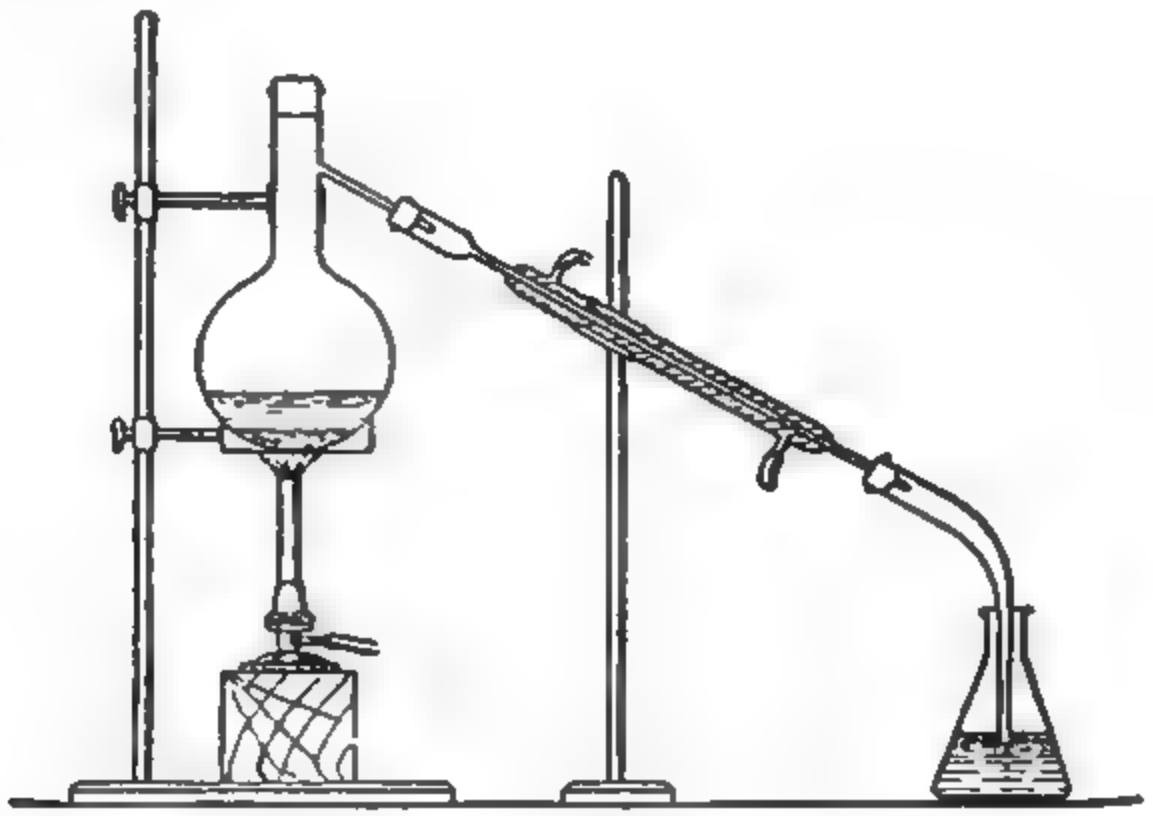


Fig. 2. Preparation of Ethyl Bromide.

Ethyl bromide is a colourless, pleasant-smelling liquid (b.p. 38°).

8. Ethyl Iodide, C_2H_5I. is prepared by gradually adding iodine to a mixture of ethyl and red phosphorus, and distilling the reaction product from a water bath.

$$2P + 3I_2 \rightarrow 2PI_3$$
$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$$
$$2P + 3I_2 + 6C_2H_5OH \rightarrow 6C_2H_5I + 2H_3PO_3$$

Expt. 2. *Preparation of Ethyl Iodide:—*

Materials required: Absolute alcohol, 25 ml.
Iodine (finely powdered), 30 gm.
Red Phosphorus, 3 gm.

Procedure. Place the alcohol and the red phosphorus in a 100 ml. round-bottom flask (Fig. 3). Fit up the latter with a reflux condenser through which a stream of cold water is passing. Remove the reflux condenser for a moment, add a small quantity (2—3 gms.) of iodine, immediately replace the reflux condenser and shake. Repeat the addition of small quantities of iodine in the same way. In case, during the addition of iodine, the reaction becomes too violent (boils), cool the flask under the tap, until the reaction has subsided. When all the iodine has been added, heat the reaction mixture on a water bath, with the reflux condenser, still on, for 1½ hours. Keep a stream of cold water running through the condenser all the time.

Cool the flask under the tap. Connect it to a Liebig condenser and an adapter, as shown in Fig. 4. Distil from a water bath until no more liquid passes over.

Transfer the distillate to a separating funnel and add about 20 ml. of water, shake well and allow to stand till it separates into two layers. Draw the lower layer of ethyl iodide into a small beaker. Discard the top layer, and pour the contents of the beaker into the separating funnel. Add about 10 ml. of a dilute solution of caustic soda, and shake thoroughly. Allow the liquid to separate again.

Draw off the lower layer of ethyl iodide into a small dry flask. Add about one gram of fused calcium chloride, and fit a well softened cork into the neck of the flask. Allow to stand until the liquid is quite clear.

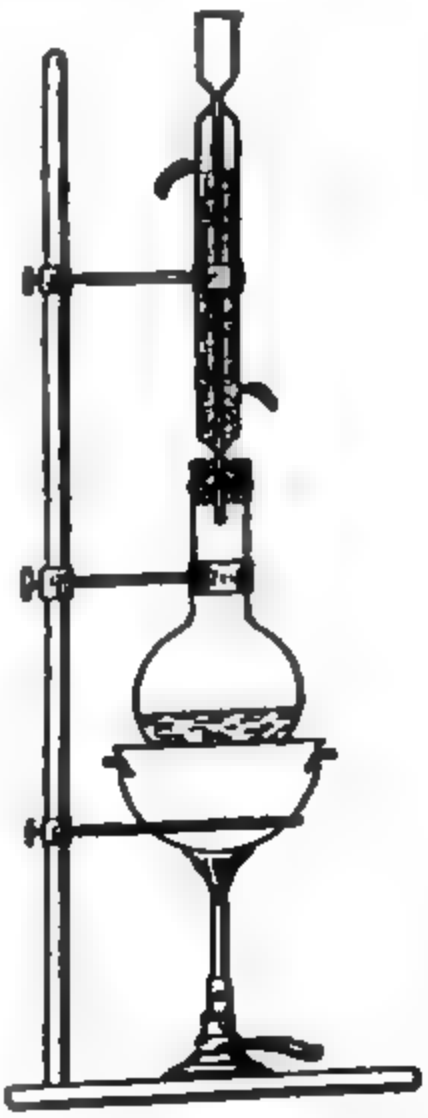


Fig. 3. Heating the reaction mixture under a Reflux Condenser.

Filter the clear liquid through a plug of glass wool into a dry, 50 ml. distillation flask. Be sure that none of the calcium chloride (solid or solution) goes along with ethyl iodide. Fit the distillation flask with a thermometer, connect the tube to a Liebig condenser, and distil the ethyl iodide. Collect the fraction boiling at 71—73° C in a small dry bottle, and stopper the latter.

Ethyl iodide is used in the synthesis of organic compounds in preference to ethyl chloride. The ease with which it can be handled and its greater reactivity more than make up for its greater cost.

9. Dihalogen Derivatives. The dihalogen derivatives of the paraffins may be divided into *two groups*, according as the two halogen atoms are in union with the same or with different carbon atoms. The latter class is obtained by the direct combination of a halogen with an olefine hydrocarbon,

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + Br_2 \longrightarrow \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br}$$

while the former may be prepared either from an acetylene hydrocarbon by making it combine with two molecular proportions of a halogen hydride.

$$\underset{\text{Acetylene}}{CH \equiv CH} + 2HBr \longrightarrow \underset{\text{Ethylidene bromide}}{CH_3.CHBr_2}$$

or from an aldehyde or a ketone by the action of phosphorus pentahalide,

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} + PCl_5 \longrightarrow \underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} + POCl_3$$

On being heated with aqueous alkalies, the derivatives containing the halogen atoms linked to two different carbon atoms yield dihydric alcohols or glycols,

$$\underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br} + 2KOH \rightarrow \underset{\text{Ethylene glycol}}{CH_2OH.CH_2OH} + 2KBr,$$

while the other group yield aldehydes or ketones:

$$\underset{\text{Ethylidene bromide}}{CH_3.CHBr_2} \xrightarrow{H.OH} \underset{\text{Unstable}}{CH_3.CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\underset{\text{2, 2-Dichloropropane}}{CH_3.CCl_2.CH_3} \xrightarrow{H.OH} \underset{\substack{\text{Dihydroxy compound}\\ \text{(unstable)}}}{CH_3.C(OH)_2CH_2} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

10. Dichloro-methane or **methylene chloride**, CH_2Cl_2. This compound may be prepared by one of the following methods :—

(1) By the action of phosphorus pentachloride on formaldehyde,

$$\underset{\text{Formaldehyde}}{H.CHO} + PCl_5 \rightarrow \underset{\substack{\text{Methylene}\\ \text{chloride}}}{CH_2Cl_2} + POCl_3$$

(2) By further chlorination of methyl chloride.

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl.$$

(3) By the reduction of chloroform by means of zinc-copper couple (compare preparation of ethane from ethyl iodide) :—

$$\underset{\text{Chloroform}}{CHCl_3} + 2H \rightarrow CH_2Cl_2 + HCl$$

Properties. (1) Methylene chloride is a colourless liquid (b.p. 42°).

(2) When submitted to hydrolysis, it yields formaldehyde,

$$CH_2Cl_2 + 2H.OH \longrightarrow \underset{\substack{\text{Unstable}\\ \text{dihydroxy compound}}}{CH_2(OH)_2} \xrightarrow{-H_2O} \underset{\text{Formaldehyde}}{H.CHO}$$

(3) On reduction with zinc-copper couple, it gives first methyl chloride and then methane :

$$CH_2Cl_2 + 2H \rightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + 2H \rightarrow \underset{\text{Methane}}{CH_4} + HCl$$

(4) On chlorination, it yields chloroform and finally carbon tetrachloride :

$$\underset{\text{Methylene chloride}}{CH_2Cl_2} \rightarrow \underset{\text{Chloroform}}{CHCl_3} \rightarrow \underset{\text{Carbon tetrachloride}}{CCl_4}$$

11. Dichloro-ethane, $C_2H_4Cl_2$, **exists in the following two forms:**

(1) **Ethylene chloride,** $\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$, **is prepared from ethylene by the direct addition of chlorine,**

$$\begin{matrix}CH_2\\\|\\CH_2\end{matrix} + Cl_2 \rightarrow \begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$$

It is a colourless liquid boiling at 84°. When submitted to hydrolysis, it gives ethylene glycol.

$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} + 2KOH \rightarrow \underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + 2KCl$$

(2) **Ethylidene chloride,** $CH_3.CHCl_2$, **is prepared by the action of** phosphorous pentachloride on acetaldehyde,

$$CH_3.CHO + PCl_5 \rightarrow CH_3CHCl_2 + POCl_3.$$

It is a colourless liquid boiling at 57. It differs from ethylene chloride in the fact that when submitted to hydrolysis it gives acetaldehyde :

$$\underset{\substack{\text{Ethylidene}\\\text{chloride}}}{CH_3.CHCl_2} \xrightarrow{H.OH} \underset{\substack{\text{Unstable intermediate}\\\text{product}}}{CH_3.CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

Prolonged treatment with chlorine converts both ethylene chloride and ethylidene chloride finally into hexachloroethane C_2Cl_6, while reduction with zinc-copper couple gives, in each case, ethyl chloride and finally ethane.

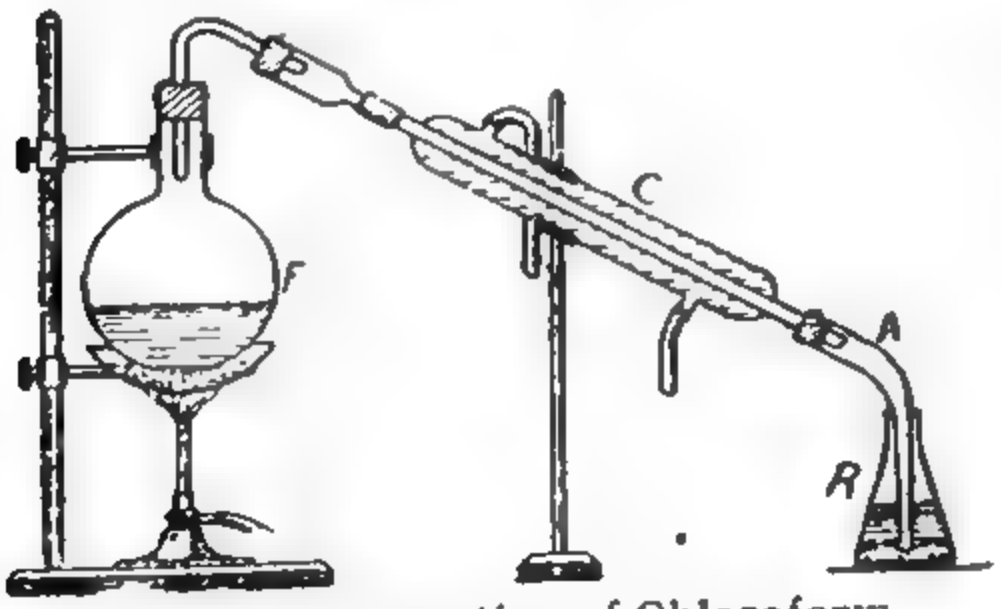


Fig 4. Preparation of Chloroform.

Constitution. The constitution of ethylene chloride and that of ethylidene chloride follow from their respective methods of preparation and behaviour on hydrolysis.

12. Trihalogen Derivatives. Of the trihalogen derivatives of paraffin hydrocarbons, the most important are : (1) Chloroform, $CHCl_3$, and (2) Iodoform, CHI_3.

13. Chloroform, or *Trichloromethane,* $CHCl_3$.

Preparation. Chloroform is prepared both on a commercial scale and in the laboratary by distilling alcohol or acetone with bleaching powder.

Expt. 3. 100 grams of bleaching powder are rubbed into a paste with about 400 c.c. of water and placed in a wo-litre flask, fitted with a condenser and adapter and a receiver (Fig. 4). 25 ml. of alcohol or acetone are added and the mixture gradually heated on a sand bath. If there are any signs of frothing, the flame should be temporarily removed, until the reaction moderates. The heating is continued, until no more chloroform distils over. The product is separated from the aqueous layer, shaken with dilute alkali, dried over calcium chloride, and redistilled.

The mechanism of the reaction in the case of alcohol is assumed to be as follows :—

Step I. Ethyl alcohol is oxidized by chlorine of the bleaching powder to acetaldehyde :

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

Step II. The acetaldehyde gets chlorinated to trichloroacetaldehyde (chloral).

$$CH_3.CHO + 3Cl_2 \rightarrow \underset{\text{Chloral}}{CCl_3.CHO} + 3HCl$$

Step III. The chloral is hydrolysed by the lime present in bleaching powder to cloroform and formic acid, the latter combining with lime to form calcium formate :

$$CCl_3.CHO + H.OH \rightarrow CHCl_3 + HCOOH \qquad [\times 2]$$
$$2HCOOH + Ca(OH)_2 \rightarrow (HCOO)_2Ca + 2H_2O$$
$$\overline{2CCl_3.CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca}$$

In the case of acetone, a similar explanation is offered :—

$$\underset{\text{Acetone}}{OC<^{CH_3}_{CH_3}} \xrightarrow{\text{Chlorination}} \underset{\text{Trichloro-acetone}}{OC<^{CH_3}_{CCl_3}} \xrightarrow{HOH} \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Preparation of Pure Chloroform. Chloroform prepared as above is generally impure. A convenient though expensive method of preparing pure chloroform consists in heating chloral or chloral hydrate with a solution of caustic soda .

$$\underset{\text{Chloral}}{CCl_3.CHO} + NaOH \rightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sodium formate}}{HCOONa}$$

Physical Properties. Chloroform is a colourless liquid having a sweet, sickly odour and a sp. gr. of 1·5 at 15°. It boils at 61°, and burns with a green-edged flame. It is soluble in about 200 volumes of cold water, to which it imparts a sweet taste.

Reactions The more important reactions of chloroform are :—

(1) *Oxidation.* Under the influence of air and light, chloroform is decomposed into hydrogen chloride and the highly poisonous gas carbonyl chlo :—

$$CHCl_3 + O \dashrightarrow \underset{\text{Carbonyl chloride}}{COCl_2} + HCl$$

(2) *Hydrolysis.* When heated with alcoholic potash under a reflux condenser, chloroform is hydrolysed into potassium formate and potassium chloride, which may be identified in the usual manner.

$$CHCl_3 + 3H.OH \longrightarrow HC(OH)_3 + 3HCl$$
$$HC(OH)_3 \longrightarrow HCOOH + H_2O$$
$$HCOOH + KOH \longrightarrow HCOOK + H_2O$$
$$HCl + KOH \longrightarrow KCl + H_2O \qquad [\times 3]$$
$$\overline{CHCl_3 + 4KOH \longrightarrow HCOOK + 3KCl + 2H_2O}$$

(3) **Carbylamine Reaction.** When a drop of chloroform is warmed with a drop of aniline and a few drops of alcoholic potash, a disgusting odour of phenyl isocyanide or carbylamine, C_6H_5NC, is developed :—

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

(4) *Chlorination.* When treated with chlorine, it gives carbon tetrachloridet,

$$CHCl_3 + Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

(5) *Reduction.* When reduced with zinc-copper couple and alcohol, chloroform is converted sucessively into methylere chloride, CH_2Cl_2, methyl chloride, CH_3Cl, and methane, CH_4.

Tests. Reactions (2) and (3) are both employed as tests for chloroform. The latter is extraordinarily sensitive and will detect 1 part of the chloroform in 5,000 parts of alcohol. It is however, not conclusive, as it is also given by bromoform. iodoform, chloral, trichloroacetic acid, and other substances that yield chloroform in the presence of an alkali.

In the case of reaction (2) a few drops of the products of hydrolysis is tested for the chloride radical with silver nitrate ; the remainder is then neutralized exactly and heated with mercuric chloride solution. The formation of a precipitate of mercurous chloride and metallic mercury shows the presence of a formate.

Tests for Impurities. Chloroform for anaesthetic purpose must be of the highest degree of purity. When shaken with water, the aqueous layer should not turn blue litmus red, nor should it give any cloudiness with silver nitrate. Further, it should not turn yellow when agitated for one hour with concentrated sulphuric acid : if the colour change occurs, it shows the presence of aldehyde, methyl alcohol, etc.

Storing of Chloroform. To avoid of oxidation, (*see* Reaction 1), the following **precautions** must be taken in storing chloroform for use as an anæsthetic :—

(*i*) It is mixed with about 1 per cent. of ethyl alcohol which serves as a retarder.

(*ii*) The bottles must be filled to the stopper. This serves to exclude air.

(*iii*) It is kept in the dark, or in bottles of amber colour.

Uses. Chloroform is used :—

(1) as an anæsthetic.

(2) as a preservative for animal or vegetable infusions and decoctions.

(3) as a flavouring agent to disguise the taste of nauseous medicines, and

(4) as a solvent for organic substances, both in the laboratory and industry.

14. Iodoform, *Tri-iodomethane*, CHI_3.

Preparation (1) Iodoform is prepared, both in the laboratory and on the commercial scale, by warming a mixture of iodine, alcohol and sodium carbonate.

$$C_2H_5OH + 4I_2 + 3Na_2CO_3 \rightarrow CHI_3 + HCOONa + 5NaI + 2H_2O + 3CO_2$$

The mechanism of the reaction is assumed to be similar to that given above for chloroform. The intermediate compound iodal, $CI_3.CHO$, analogous to *chloral*, has not been isolated.

Expt. 4. *Preparation of Iodoform.*

Sodium carbonate crystals, 20 gm.
Ethyl alcohol, or acetone, 5 gm.
Water 60 ml.
Iodine, 10 gm.

Dissolve the sodium carbonate and alcohol (or acetone) in water, and giadually add the iodine to the solution. During the addition, the temperature is gradually raised to 80°, but not higher as iodoform is readily hydrolysed. When the deep brown colour of iodine has disappeared, the liquid is allowed to cool and csystals of iodoform filtered. They are then washed with a little distilled water and finally purified by recrystallization from alcohol.

(2) A modern method of preparing iodoform consists in electrolysing an aqueous-alcoholic solution of potassium iodide and carbonate.

Properties. Iodoform crystallizes in lustrous, yellow, sixsided plates, having a strong, characteristic smell, and melting at 119°C. It sublimes readily, and is volatile at ordinary temperatures. It is insoluble in water, but soluble in alcohol and ether.

In its chemical behaviour, iodoform is similar to chloroform. It gives the carbylamine reaction, and is hydrolysed by caustic potash, yielding potassium iodide and potasium formate. On reduction with hydriodic acid and phosphorus, it gives methylene iodide, CH_2I_2.

Use. Iodoform is much used in surgery as an antiseptic

15. Carbon Tetrachloride. Carbon tetrachloride or *tetrachloromethane*, CCl_4, is obtained on a commercial scale by the chlorination of carbon disulphide in the presence of anhydrous aluminium chloride, iron or iodine (which act as chlorine carriers) :

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

Sulphur monochloride (b.p. 138°), which is here obtained as a by-product is separated by fractional distillation. The carbon tetrachloride fraction is further purified by shaking with caustic soda and distillation. Carbon tetrachloride is a colourless liquid boiling at 78°.

It is used on a large scale as a solvent, and in medicine for exterminating intestinal worms. The use of carbon tetrachloride in putting out oil fires is illustrated in the following experiment.

Expt. 5. Place some kerosene oil in a small dish, and set fire to it. Now pour a little carbon tetrachloride over the burning oil; the flame is at once extinguished.

QUESTIONS

1. Describe the preparation of Ethyl Bromide in the laboratory, and draw a neat sketch of the apparatus. Give the various important reactions of this compound.
2. How may Ethyl Bromide be obtained from (*a*) Ethane, and (*b*) Ethylene and how could it be reconverted into these hydrocarbons? Explain, by means of structural formulæ, the relationship existing between these three compounds.
3. "Aliphatic mono-halogen derivatives provide a powerful synthetic instrument in the hands of organic chemist." Illustrate this statement by giving outstanding reactions of this class of substances. (*East. Punjab Inter.. 1948.*)
4. Describe two different reactions by which it is possible to ascend a homologous series. By what series of reactions may methyl alcohol be converted into ethyl alcohol ?
5. What is the action of boiling, aqueous solution of potash on Ethyl Iodide. Would it make any difference if alcoholic potash is used instead of aqueous potash ? (*Unit. Prov., Inter., 1928*)

6. Explain the meaning of the term *hydrolysis*. Give one example. (*Ajmer, Inter., 1932*)

7. How is chloroform prepared on the laboratory scale? What happens when it is acted upon with —(*a*) chlorine, (*b*) sodium hydroxide, (*c*) sodium hydroxide and aniline? Mention the chief uses of chloroform. (*Punjab. Inter., 1947*)

8. If a small quantity of pure chloroform is exposed to sunlight in a large, colourless glass bottle, would the chloroform still remain pure, and if not, how would you prove it? (*Unit. Prov. Inter., 1925*)

9. Describe with necessary experimental details, the preparation of choloform. What tests would you apply to identify chloroform? What precautions must be observed in storing chloroform for use as an anæsthetic? (*Punjab, Inter., 1933*)

10. What is Iodoform? How is it prepared in the laboratory, and how is it manufactured commercially? Describe its properties. What is the action on it of boiling alcoholic potash? (*Unit. Prov. Inter., 1926*)

11. Describe briefly, giving equations, the reactions which take place between the following substances :—

(*i*) A watery paste of bleaching powder and acetone :
(*ii*) Iodoform and caustic soda. (*Unit. Prov. Inter., 1932*)

12. How will you bring about the following conversions? :—

(*i*) chloroform into formic acid ;
(*ii*) chloroform into methane ;
(*iii*) chloroform into carbon tetrachloride ;
(*iv*) Ethyl bromide into ethyl magnesium bromide.

13. Write short notes on :—

(*i*) Carbylamine reaction ;
(*ii*) Grignard's reagents ;
(*iii*) Alkyl halides.

14. What structural relationship exists between methane, chloroform, and odoform? Write structural formulæ of these compounds to illustrate your explanation.

15. An organic liquid analysed C=10·06, H=0·84, Cl=89·1 percent. Its vapour density was 60. When this substance was heated with aniline and alcoholic potash, it gave a pungent bad smell. What was the substance? (C=12; H=1, Cl=35·5) (*Ans.* Chloroform, $CHCl_3$) (*Punjab, Inter., 1930*)

16. The bromo derivative of a paraffin when analysed gave the following results :

(*a*) 0·109 gm. of the substance gave 0·088 gm. of carbon dioxide and 0·045 gm. of water.

(*b*) 0·185 gm. of the same substance gave 0·319 gm. of the silver bromide. Find the molecular formula of the compound [*Ans.* C_2H_5Br.] (*Bombay, Inter., 1931*)

17. Two liquids, one boiling at 83°C and the other at 57°C, gave, on analysis, the same results, *viz.*, 0·2376 gm. gave, on combustion, 0·2112 gm. CO_2 and 0·0864 gm. H_2O ; 0·121 gm. gave, when heated with silver nitrate and nitric acid, 0·351 gm. AgCl. Calculate the simplest formula for these substances. How do you account for two substances having the same composition, and what do you regard as the true formula of each compound? (*Punjab, Inter., 1944*)
(C=12 ; Cl=55·5 ; Ag=108)

CHAPTER 10

MONOHYDRIC ALCOHOLS

1. General. Alcohols are derived from aliphatic hydrocarbons by the replacement of one or more atoms of hydrogen by hydroxyl groups. They are termed **monohydric, dihydric** or **trihydric,** according to the number of hydroxyl groups present in the molecule. The most important series of monohydric alcohols is that derived from the paraffin hydrocarbons, and possesses the **general formula,,** $C_nH_{2n+1}OH$, or $C_nH_{2n+2}O$.

2. Nomenclature and Isomerism. The monohydric alcohols, like the monohalogen derivatives of paraffin hydrocarbons, are usually named after the **alkyl** group that they contain. The Geneva names are derived from those of the hydrocarbons by changing the terminal *-e* into- *ol*. A third method consists in regarding them as derivatives of methyl alcohols, CH_3OH, or **carbinol,** as it is termed in this connection.

Monohydric alcohols are divided into **primary, secondary.** and **tertiary alcohols.** The primary alcohols contain the monovalent group—CH_2OH, the secondary alcohols contain the divalent group $>CHOH$, while the tertiary alcohols contain the trivalent group $-\overset{|}{\underset{|}{C}}-OH$.

Hence they may be regarded as derived from methyl alcohol or *carbinol*, CH_3OH, by the substitution of respectively one, two and three hydrogen atoms by alkyl groups.

We may now consider the number ef alcohols derived from the different paraffin hydrocarbons. Methane CH_4 and ethane, $CH_3.CH_3$, since they contain hydrogen only in one form of combination, give rise to only one monohydric alcohol each :—

CH_3OH, Methyl alcohol, methanol, or carbinol,

C_2H_5OH, Ethyl alcohol, ethanol, methyl carbinol.

Propane, $CH_3\ CH_2.CH_3$, gives two isomeric alcohols, of which one is primary and the other seoondary :—

(*i*) $CH_3.CH_2.CH_2\,OH$, *Normal* propyl alcohol, propanol-1 or ethyl carbinol.

(*ii*) $CH_3.CH_2.(OH).CH_3$, Isopropyl alcohol, propanol-2, or dimethyl carbinol.

Normal butane, $CH_3.CH_2.CH_2.CH_3$, gives rise to two (1 and 2), and isobutane, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CH_3$, to two more (3 and 4) monohydric alcohols. Of these four **butyl alcohols,** two are primary, one secondary and one tertiary :—

(1) $CH_3.CH_2.CH_2.CH_2OH$
Normal primary butyl alcohol, 1-Butanol, *n*-propyl carbinol

(2) $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CH_2OH$
Isobutyl alcohol, 2 methyl 3-propanol, isopropyl carbinol

(3) $CH_3.CH_2.CH(OH).CH_3$
Normal secondary butyl alcohol 2-Butanol, methyl ethyl carbinol,

(4) $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>\!C.OH$
Tertiary butyl alcohol trimethyl carbinol

3. General Methods of Preparation. Monohydric alcohols

derived from saturated hydrocarbons can be obtained by the following general methods :—

(1) *By the Hydrolysis of Alkyl Halides.* When an alkyl halide is brought into contact with silver hydroxide, or boiled with an aqueous solution of an alkali hydroxide it is converted into an alcohol :—

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + AgOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + AgBr$$

Since the alkyl halides can be obtained from *paraffin hydrocarbons* by substitution, and also from the *olefines* by the direct addition of a halogen acid, the aliphatic alcohol may be indirectly produced from these hydrocarbons ; *e.g.*,

$$\underset{\text{Methane}}{CH_4} \xrightarrow{\text{Chlorination}} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{AgOH} \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{+HI} \underset{\text{Ethyl iodide}}{CH_3.CH_2I} \xrightarrow{AgOH} \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

(2) *By the Hydrolysis of Esters.* When an ester is boiled with an alkali, it is hydrolysed to give an alcohol :—

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + KOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + CH_3COOK$$

The method is chiefly employed for preparing certain *higher alcohols* present in ethereal oils occurring in nature. The preparation of glycerol from fats and oils is another important example.

(3) *By the Reduction of Aldehydes and Ketones.* Aldehydes and ketones, on reduction with nascent hydrogen (sodium amalgam and very dilute sulphuric acid), give primary and secondary alcohols respectively ; *e.g.*,

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} + 2H \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2H \longrightarrow \underset{\text{Isopropyl alcohol}}{CH_3.CH(OH).CH_3}$$

(4) *By the Reduction of Acid Chlorides and Anhydrides.* These compounds when reduced with sodium amalgam and very dilute sulphuric acid yield primary alcohols ; *e.g.*,

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + 4H \rightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + HCl$$

(5) *By the Action of Nitrous Acid on a Primary Amine.* When a primary amine is treated with nitrous acid ($NaNO_2+HCl$), the NH_2 group gets replaced by an OH group, and an alcohol is produced. Thus ethylamine gives ethyl alcohol :—

$$\underset{+NO\ OH}{C_2H_5NH_2} \rightarrow C_2H_5OH + N_2 + H_2O$$

(6) By the fermentation of certain carbohydrates ; *e.g.*,

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

This method, though not very general, is of great commercial importance.

4. Physical Properties. Lower alcohols are colourless mobile liquids having a characteristic spirituous odour and a burning taste.

Higher homologues are tasteless and odourless.

In most of the organic solvents, the alcohols are miscibie in all proportions. The first three members are soluble in water, but with the higher members the solubility rapidly decreases.

General Reactions. All alcohols give the first four reactions described under methyl and ethyl alcohols. The reaction given in the following section differentiate primary, secondary and tertiary alcohols from one another.

5. Distinction between Primary, Secondary and Tertiary Alcohol :—

(1) *Behaviour on oxidation.* On oxidation, primary alcohols give at first aldehydes and then acids containing the *same* number of carbon atoms as the original alcohol ; *e.g.*,

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \xrightarrow{-2H} \underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow{+O} \underset{\text{Acetic acid}}{CH_3.COOH}$$

Secondary alcohols give ketones containing the *same* number of carbon atoms :—

$$\underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH} \xrightarrow{-2H} \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO}$$

Tertiary alcohols, since they contain no hydrogen directly linked to the hydroxyl-bearing carbon atom, do not readily undergo oxidation. On prolonged treatment with strong oxidizing agents, the molecule *breaks up*, yielding ketones and carboxylic acids, each containing a *smaller* number of carbon atoms than the alcohol itself. Thus, trimethyl carbinol, $(CH_3)_3C.OH$, on vigorous oxidation, yields acetone, acetic acid, and carbonic acid :—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\!\!<\!\!\begin{matrix}CH_3\\OH\end{matrix} + 4O \rightarrow \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO} + CO_2 + 2H_2O \quad (i)$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\!\!<\!\!\begin{matrix}CH_3\\OH\end{matrix} + 8O \rightarrow \underset{\text{Acetic acid}}{CH_3.C\!\leqslant\!\!\begin{matrix}OH\\O\end{matrix}} + 2CO_2 + 3H_2O \quad (ii)$$

In these reactions, an oxygen atom enters the molecule of a tertiary alcohol, attaching itself to the carbon atom carrying the hydroxyl group and driving out from the molecule either one alkyl and one hydroxyl group [(*see* equation (*i*)] or two alkyl groups [*see* equation (*ii*)]

(2) *Action of Hot, Reduced Copper.* When the vapour of an alcohol is passed over reduced copper heated at 300°, different products are obtained according to the nature of the alcohol. If it be primary, it yields an aldehyde and hydrogen,

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2,$$

if secondary, a ketone and hydrogen,

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \rightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + H_2$$

and if tertiary, an olefine and water,

$$\underset{\text{Trimethyl carbinol}}{\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH).CH_3} \rightarrow \underset{\text{Unsymmetrical dimethyl-ethylene}}{\begin{matrix}CH_3\\CH_3\end{matrix}>C=CH_2} + H_2O$$

(3) **Victor Meyer's Method.** An indirect method of distinguishing between a primary, a secondary and a tertiary alcohol is to first convert it into the corresponding *nitroparaffin*. This is done by treating the alcohol with iodine and red phosphorus, when an alkyl iodide is formed. The latter when distilled with silver nitrate yields the corresponding nitroparaffin.

The nitroparaffin, thus obtained, is dissolved in potassium hydroxide solution, sodium nitrite is added, the solution is acidified with dilute sulphuric acid, and then again made alkaline. The production of a blood-red coloration shows it to be a primary, a blue coloration a secondary, and no coloration a tertiary alcohol. The distinction is based on the different behaviour of the corresponding nitroparaffins towards nitrous acid :—

The primary nitroparaffins react with nitrous acid, yielding **nitrolic acids,** which dissolve in alkalies to give dark-red solutions :

$$\begin{matrix}RCH_2NO_2\\+\ O\ \ NOH\end{matrix} \rightarrow \underset{\text{nitrolic acid}}{\begin{matrix}RC.NO_2\\\|\\NOH\end{matrix}} \xrightarrow{KOH} \underset{\text{potassium salt (dark-red)}}{\begin{matrix}RC.NO_2\\|\\NOK\end{matrix}}$$

The secondary nitroparaffins react with nitrous acid, yielding blue-coloured nitro-nitroso compounds, called **pseudo-nitrols,** which dissolve in ether to give blue-coloured solutions :—

$$\begin{matrix}R_2C\ \ H\\+\ HO\ NO\end{matrix} \rightarrow \underset{\text{pseudo-nitrol}}{\begin{matrix}R_2C.NO_2\\|\\NO\end{matrix}} + H_2O$$

The tertiary nitroparaffins, since they contain no hydrogen directly linked to the carbon carrying the nitro group, do *not* react with nitrous acid.

6. Methyl Alcohol, *Methanol*, or *Wood Spirit*, CH_3OH.

Occurrence. Methyl alcohol occurs as methyl salicylate in oil of wintergreen and as methyl benzoate in oil of cloves.

Formation. Methyl alcohol may be obtained by the following reactions :—

(1) *By Hydrolysis of Methyl Iodide.* When methyl iodide, CH_3I, is boiled with an aqueous solution of sodium hydroxide, or treated with silver hydroxide in the cold, it yields methyl alcohol :

$$CH_3I + NaOH \rightarrow CH_3OH + NaI$$
$$CH_3I + AgOH \rightarrow CH_3OH + AgI$$

(2) *By Hydrolysis of Methyl Acetate.* When methyl acetate (or any other methyl ester) is boiled with an aqueous solution of an alkali it yields methyl alcohol :

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

(3) *By Reduction of Formaldehyde.* When formaldehyde is treated

with nascent hydrogen (sodium amalgam and very dilute sulphuric acid) it gets reduced to methyl alcohol :

$$\underset{\text{Formaldehyde}}{H.CHO} + 2H \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH}$$

(4) *By Action of Nitrous Acid on Methylamine.* When methylamine dissolved in an excess of hydrochloric acid is treated with sodium nitrite, we get methyl alcohol. The reaction occurs in two steps :—

$$\underset{\text{Sodium nitrite}}{NaNO_2} + HCl \rightarrow NaCl + \underset{\text{Nitrous acid}}{HNO_2}$$

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Nitrous acid}}{ONOH} \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + N_2 + H_2O$$

Manufacture. Methyl alcohol is manufactured by two different methods :—

(1) **By destructive Distillation of Wood.** The distillation of wood is usually carried out in large, horizontal retorts made of boiler plates (Fig. 1). The wood, after being cut into pieces of suitable size, is put into wire-work case mounted on wheels, which can be rolled in or out of the retorts as desired. The heating is effected by means of wood gas obtained during the process. As soon as the distillate begins to flow from the end of the condenser, the fire is turned low, as over-heating causes a loss in volatile matter. Towards the end, the temperature is raised quite rapidly in order to drive out the heavy tars. The products of distillation are (*i*) **wood gas** consisting mainly of CO, CH_4 and H_2, (*ii*) an aqueous layer, known as **pyroligneous acid,** which, in addition to a large proportion of water, contains acetic **acid**, acetone, and methyl alcohol, and (*iii*) **wood tar.** The residue consists of **charcoal**

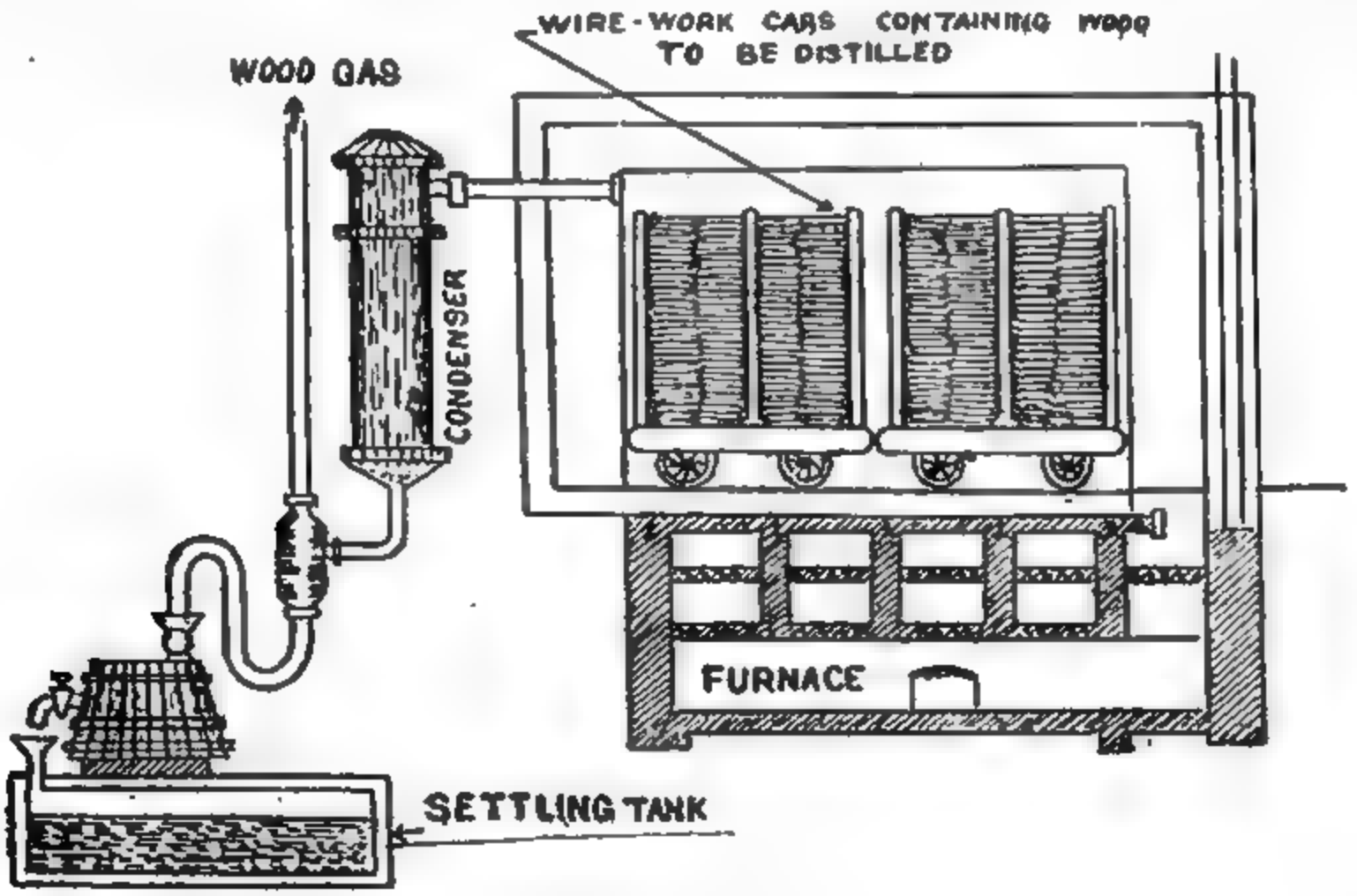


Fig. 1. Plant for the Distillation of Wood.

which is removed at the end of the operation when still hot, thus saving the heat of the brickwork for the next charge.

The pyroligneous acid, which forms the upper layer, is run off from the wood tar and distilled. The vapours are passed through hot milk of lime, which retains acetic acid as calcium acetate, while the methyl

alcohol and acetone, together with water, pass on.

The distillate, after being dehydrated with quicklime, is fractionated to obtain acetone (b. p. 56°) and methyl alcohol (b p. 65°).

Expt. 1 *Destructive Distillation of Wood.* Fit up the apparatus shown in Fig. 2. Put some saw-dust in the test-tube, and heat the latter by means of a burner. The distillate that collects in the bottle will consist of: (*i*) pyroligneous acid (upper layer), and (*ii*) wood-tar (lower layer). The escaping gas (wood gas) maybe lighted at the upper end of the straight piece of glass tubing. The residue in the test-tube is charcoal.

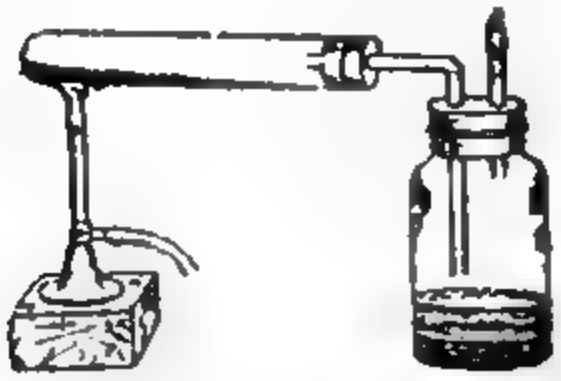


Fig. 2. Destructive Distillation of Wood.

(2) **From Water Gas (Patart Process).** Since 1923, large quantity of methyl alcohol are being produced synthetically. The process consists in passing a mixture of water gas ($CO + H_2$) and hydrogen under a high pressure (200 atoms), over a catalyst, consisting of zinc oxide mixed with finely divided copper heated to 450° :

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

Physical Properties. Pure methyl alcohol is a colourless liquid, which boils at 65°. It possesses an agreeable. wine-like odour and burning taste, but is poisonous. Many cases of blindness or death have been caused by drinking mixtures containing methyl alcohol. Bindness may also result from prolonged exposure to its vapours. It is miscible with water in all proportions.

Reactions:—

(1) *Reaction with Metallic Sodium.* When treated with metallic sodium (or potassium), the hydrogen of the hydroxyl group is replaced by the metal :—

$$\underset{\text{Methyl alcohol}}{2CH_3OH} + 2Na \rightarrow \underset{\text{Sodium methoxide}}{2CH_3ONa} + H_2$$

(2) *Reaction with Phosphorus Pentachloride or Trichloride.* When methyl alcohol is treated with phosphorus pentachloride, PCl_5 or phosphorus trichloride, PCl_3, the hydroxyl group is replaced by chlorine:—

$$\underset{\text{Methyl alcohol}}{CH_3OH} + PCl_5 \rightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + \underset{\text{Phosphorus oxychloride}}{POCl_3} + HCl$$

$$3CH_3OH + 2PCl_3 \rightarrow 3CH_3Cl + P_2O_3 + 3HCl$$

(3) *Esterification.* When methyl alcohol is treated with gaseous hydrogen chloride in the presence of anhydrous zinc chloride, it yields methyl acetate:—

$$CH_3OH + HCl \rightleftharpoons \underset{\text{Methyl chloride}}{CH_3Cl} + H_2O$$

The zinc chloride serves to remove the water produced in the reaction, and thus prevents the back reaction.

Similarly, when the alcohol is treated with acetic acid (or any other organic acid) in the presence of concentrated sulphuric acid, it yields methyl acetate:—

$$\underset{\text{Acetic acid}}{CH_3COOH} + CH_3OH \rightleftharpoons \underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O$$

The sulphuric acid serves to remove the water produced.

Note. The compounds formed by the interaction of alcohols and acids are called esters, and the reaction, therefore, is called **esterification**. Methyl chloride and

methyl acetate are esters of methyl alcohol with hydrochloric acid and acetic acid respectively.

(4) *Action of Concentrated Sulphuric Acid.* When methyl alcohol is heated with concentrated sulphuric acid, **methyl hydrogen sulphate.** CH_3HSO_4, is first formed, which then reacts with the excess of methyl alcohol present to give **dimethyl ether** :—

$$CH_3OH + H_2SO_4 \rightleftharpoons \underset{\text{Methyl hydrogen sulphate}}{CH_3.HSO_4} + H_2O$$

$$CH_3.HSO_4 + CH_3OH \rightarrow \underset{\text{Dimethyl ether}}{CH_3O.CH_3} + H_2SO_4$$

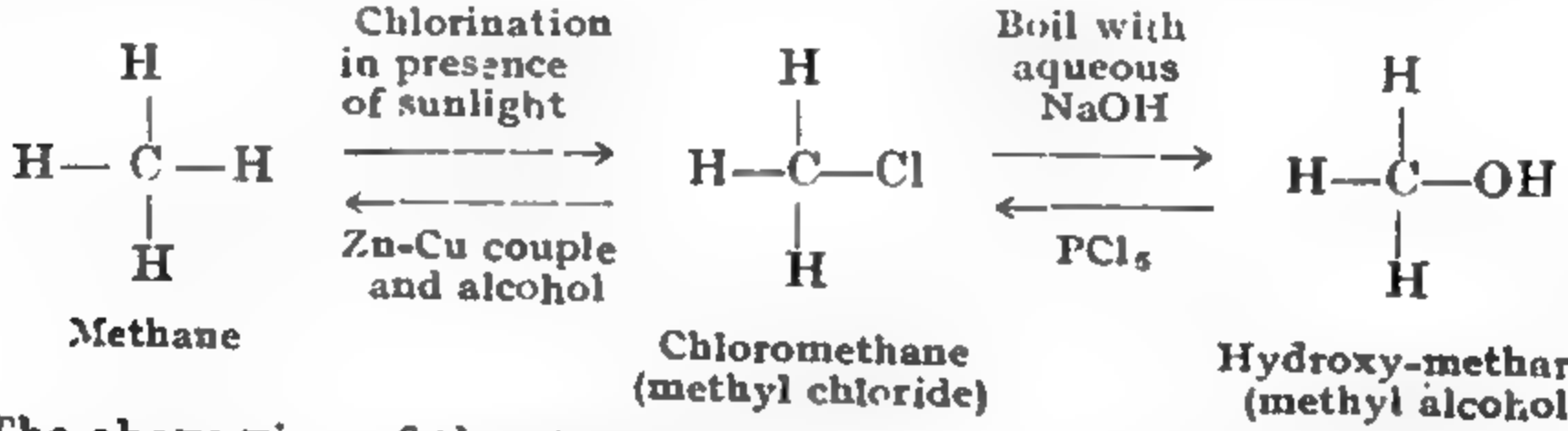
(5) *Oxidation.* When methyl alcohol is oxidized by means of cupric oxide, or by oxygen in the presence of platinum (catalyst), it yields formaldehyde :—

$$2CH_3OH + O_2 \rightarrow \underset{\text{Formaldehyde}}{2H.CHO} + 2H_2O$$

The formaldehyde when treated with mild oxidizing agents (*e.g.*, ammoniacal silver nitrate), gives formic acid :—

$$H.CHO + O \rightarrow \underset{\text{Formic acid}}{H.COOH}$$

Constitution. Methyl alcohol is a monohydroxy derivative of methane. This is proved by the interconversion of these compounds as shown below :—



The above view of the structure of methyl alcohol is further supported by the following considerations :—

(1) If hydrogen, oxygen and carbon are to be given their normal valencies there can be only one structure possible (*i.e.*, the one given above) for a compound having the molecular formula CH_4O (compare Chap. 6, Sec. 6).

(2) The reaction with metallic sodium, when only *one* of the hydrogen atoms is replaced by the metal, shows that this hydrogen atom must be in a *different* state of combination from the rest, as shown in the above formula.

(3) The reaction with phosphorus pentachloride, in which the oxygen atom is removed *together with one of the hydrogen atoms* shows that this hydrogen atom must be linked to carbon through the oxygen atom.

Detection. The presence of methyl alcohol can be readily detected by the formation of methyl salicylate or formaldehyde. It may be **differentiated from ethyl alcohol** by (*i*) its failure to give the iodoform test, and (*ii*) by its power to reduce oxidized copper coil with the production of an odour of formaldehyde (**Expt. 2,** *iii*).

Expt. 2: (*i*) Warm a few drops of methyl alcohol with a little salicylic acid and a drop or two of concentrated sulphuric acid. Noitce the characteristic, fragrant odour of methyl salicylate.

(*ii*). Repeat Expt. 3 (Sec. 14), using *pure* methyl alcohol. No iodoform can be detected.

(*iii*) Put a few drops of methyl alcohol in a bottle containing a layer of asbestos at its bottom Heat a roll of copper gauze strongly in the oxidizing flame; until it gets covered with a film of black cupric oxide, introduce it, while still hot, into the bottle, and cork the latter. Notice that the gauze is immediately reduced. On opening the cork, the pungent charateristic odour of formaldehyde will be observed.

Uses. (1) The chief use of methyl acohol is as a denaturant for ethyl alcohol.

(2) About the same quantity is oxidized to formaldehyde.

(3) Large quantities of methyl alcohol are used in the manufacture of dimethylaniline, dyes, drugs and perfumes.

7. Ethyl Alcohol, *Ethanol*, $CH_3.CH_2OH$.

Occurrence. Ethyl alcohol occurs naturally in the ferm of its esters with organic acids in many essential oils and fruits.

Formation. Ethyl alcohol may be obtained by reactions analogous to those used in the case of methyl alcohol, namely:—

(1) Hydrolysis of Ethyl Bromide (or Iodide):—

$$C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$$

(2) Hydrolysis of Ethyl Acetate:—

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(3) Reduction of Acetaldehyde:—

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2H \rightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

(4) Action of Nitrous Acid on Ethylamine:—

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + ON\ OH \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2 + H_2O$$

Manufacture. Ethyl alcohol is manufactured on a large scale from two kinds of materials: (1) saccharine materials, *e.g.*, molasses from the manufacture of cane-sugar, and (2) starchy substances, such as potatoes, barley, corn and rice.

The production of pure alcohol or *rectified spirit* consists of three main steps: (*i*) *Fermentation*, (*ii*) *Distillation*, and (*iii*) *Rectification*.

(1) **Fermentation.** Sugar can be directly subjected to alcoholic fermentation, while starch must first be converted into a sugar called *maltose*.

(*a*) **Production of Alcohol From Sugar**: In the case of saccharine materials fermentation is directly effected by means of yeast (*Saccharomyces*, see Sec. 10). The sugar is generally empolyed in the form of "molasses"—a dark-coloured, syrupy liquid obtained in the manufacture of cane sugar from which the sugar cannot be profitably extracted. Molasses is diluted with water, yeast is then added, and the mixture is placed in a warm room. The liquid soon begins to ferment and effervesce, owing to slow evolution of carbon dioxide. In about 35 to 40 hours, the action is complete, when yeast is filtered off, and the fermented liquor, technically know as the "wash" is subjected to distillation.

The reactions taking place during fermentation of sugar will be explained later (Sec. 10).

(*b*) **Production of Alcohol From Starch.** The production of alcohol

from starch consists of two distinct steps: (*i*) conversion of starch into maltose (*Saccharification*), and (*ii*) alcoholic fermentation.

(*i*) **Saccharification.** The conversion of starch into maltose is brought about by means of an enzyme, called **diastase**, which is produced during the germination of corn, and is also found in saliva and the pancreatic juice. The diastase is not used as such, but is employed together with the whole corn in the form of **malt**, which is most conveniently obtained by the germination of barley. Barely is malted by allowing it to germinate in the dark at 15°, in layers about 5 inch thick. The germination is then stopped by raising the temperature, and the malt is crushed and extracted with water. The resulting liquid, known as **malt-extract**, contains diastase in solution.

Potatoes, rice, maize, or unmalted barley are employed as the usual source of starch. They are rasped, or crushed, and then gelatinized by treatment with super-heated steam The resulting mass is mixed with water, and some malt-extract is added. The temperature is maintained at 60° to 62°C, until the conversion of starch into maltose is practically complete (about 20 minutes). The liquid is then boiled, in order to stop the action of diastase. The conversion of starch into maltose, which is a hydrolytic action, is represented by the following equation:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)x} + x\,H_2O \rightarrow \underset{\text{Maltose}}{xC_{12}H_{22}O_{11}}$$

The process is known as **mashing** and the product as *mash* or *wort*.

As an alternative, starch is converted into sugar (glucose) by means of hot, dilute sulphuric acid or by hydrochloric acid.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)x} + xH_2O \rightarrow \underset{\text{Glucose}}{xC_6H_{12}O_6}$$

(*ii*) **Alcoholic Fermentation.** The saccharine liquid obtained by either of the processes described under (*i*) is fermented by means of *yeast* at a temperature not exceeding 33° C. The fermentation takes three to four days for completion. In the case of "mash", the maltose present is first decomposed into glucose by the enzyme **maltose** contained in the yeast :

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

The glucose thus formed is at once decomposed by **zymase** — another enzyme present in yeast—giving alcohol.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2$$

During fermentation, the frothing of the liquid occurs, owing to the evolution of carbon dioxide.

In case the starch has been saccharified by means of dilute sulphuric acid or hydrochloric acid, the glucose present is directly attacked by zymase, producing alcohol.

(2) **Distillation.** The fermented liquid, which contains not more than 18 per cent of alcohol, is subjected to fractional distillation. This, in modern plants, is effected in one step and continuously

In great Britain, the fractionation is carried out in the **Coffey still** (Fig. 3) which was patented by Aeneas Coffey in 1832. It consists essentially of a combination in series of two fractionating columns known as the *analyser* and the *rectifier*. The "analyser" (shown on the left) is divided into a series of chambers by horizontal

plates, *P*, perforated with holes and furnished with valves, *V*; opening upwards. From each of these an overflow pipe *F*, passes down and dips into a shallow cup, *C*, on the next lower plate. The cup holds a sufficient amount of liquid to form a hydraulic seal at the lower end of each overflow pipe. The overflow pipes project about an inch or so above the perforated plates, thus determining the depth of the liquid layer on each plate. The lower half of the "rectifier", is also divided into chambers by perforated plates, and is provided with overflow pipes. Through the chambers of the rectifier pass coils of pipe, *A*, through which the liquid to be distilled flows on its way to the analyser.

The Coffey still works on the *counter current principle*. The liquid to be distilled passes downwards through the coils of pipes in the rectifier, where it gets heated

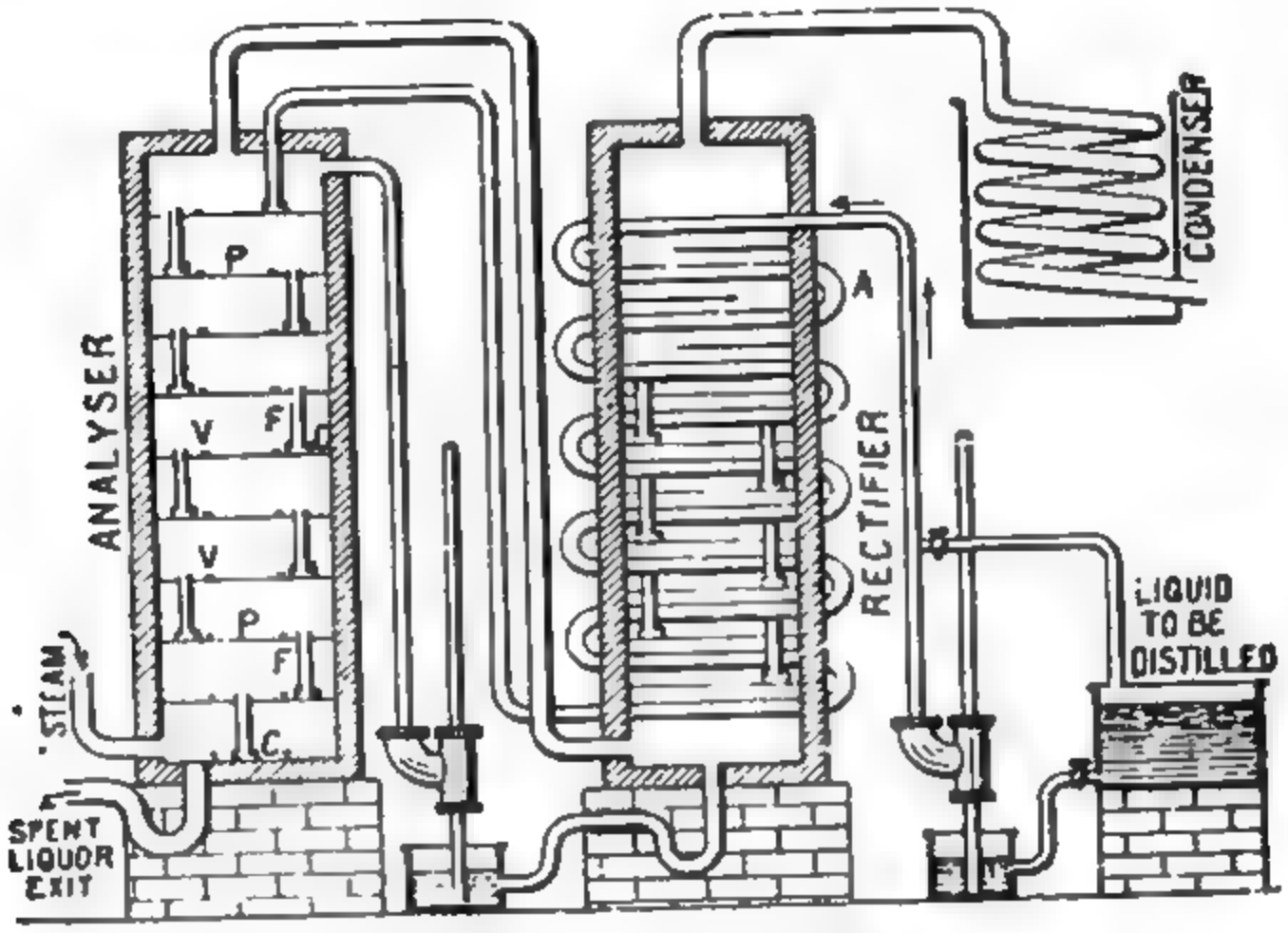


Fig. 3. Coffey Still.

(by steam and alcohol vapour) nearly to its boiling-point, and is then discharged at the top of the analyser. Free steam from a boiler is admitted at the base of the analyser, and, passing upwards through the thin layers of liquid on the perforated plates, carries with it the vapour of alcohol and other volatile substances present in the fermented liquid. In each one of the chambers there occurs an exchange of constituents between the liquid layer and the vapours; the alcohol present in the liquid evaporates while the water vapour from the gaseous phase undergoes condensation (compare Chap. 2, Sec. 10). This process is repeated in each chamber, and the ascending mixture of vapours, therefore, gets continuously richer in alcohol, while the down-coming liquid gets progressively poorer in alcohol.

The vapour of alcohol etc. passes out of the analyser at the top and then enters the rectifier at its base. During its upward passage, practically the whole of the water vapour gets condensed by a similar action to that taking place in the analyser and also by coming into contact with coils of pipe conveying the cold, fermented liquid. Hence only the alcohol vapour passes out at the top of the rectifier, and is conveyed to the condenser. The water condensed in the rectifier contains some alcohol, and is, therefore, conveyed to the top of the analyser, where it mixes with the fermented liquid. The spent liquor, entirely deprived of its volatile constituents is drawn off at the base of the analyser.

The **raw spirit** obtained by distillation contains from about 90 to 96 per cent of alcohol. The latter limit represents the constant boiling mixture of alcohol and water, whichboils at 78·3°. For industrial purposes such as when used as a fuel, or in making varnishes etc, the raw spirit is *denatured*, *i.e.*, rendered unfit for drinking, by the addition of about 10 per cent of crude methyl alcohol, and a small quantity of paraffin oil, or by the addition of rubber distillate. The product, known as **methylated spirit or denatured alcohol**, is sold duty free.

(3) **Rectification.** When required for internal use, *e.g.*, for the preparation of spirits, pharmaceutical tinctures, etc., the raw spirit must be freed from the oily mixture of higher alcohols (known as **fusel oil**[1]), that it always contains, and from low-boiling impurities, such as acetaldehyde Formerly, fusel oil was removed from the crude spirit by dilution with water and filtration through charcoal, but at the present time fractional distillation is relied upon. The crude spirit is submitted to careful fractional distillation in specially designed stills, and the following fractions are collected separately :

(*i*) *First runnings*, *i.e.*, low-boiling by-products consisting chiefly of acetaldehyde.

(*ii*) *Rectified spirit*, consisting of pure aqueous alcohol containing up to a maximum of 96 per cent ethyl alcohol.

(*iii*) *Last runnings*, which consist of 'fusel oil' (*see* Sec. 9).

8 Absolute Alcohol. By this term is meant alcohol entirely free from water. As alcohol forms a constant-boiling mixture with water, it is not possible to effect a complete separation of the two liquids by fractional distillation. Other mears must. therefore, be adopted. In the laboratory, the dehydration is effected by distillation over quicklime The last traces of moisture (about 0·5 per cent) may then be removed by treatment with a calculated amount of metallic sodium followed by redistillation.

9. By-Products of Alcohol Industry. The important by-products of the alcohol industry are :—

(1) **Carbon Dioxide.** During the fermentation, large quantities of carbon dioxide are evolved. The gas is purified and compressed to the liquid state, and is sold either as such or in the solidified form for refrigeration purposes.

(2) **Head Products.** The more volatile constituents (chiefly acetaldehyde and volatile esters) present in the crude spirit pass over as "first runnings" or "head products" during the fractional distillation of crude spirit, and are collected separately.

(3) **Fusel Oil.** This is obtained as the "*last running*" or "*tail products*" during the fractionul distillation of crude spirit. It consists of an oily mixture of higher alcohols that are only moderately soluble in water.

The proportion of fusel oil in raw spirit is from 0·2 to 0·4 per cent. by volume. It may be increased by the addition of leucine and other amino-acids to the fermenting mash.

Fusel oil fetches a much higher price per gallon than the alcohol itself. It is chiefly used in the production of *commercial* amyl alcohol which has numerous technical applications.

(4) **Spent Wash.** The "spent wash," *i.e.*, the liquid from which the alcohol has been recovered by distillation, contains all the proteins present in the starting material. It is utilized as a cattle feed.

(5) **Argol** or **Tartar.** This consists of crude potassium hydrogen tartrate, which, being insoluble in aqueous alcohol, separates during fermentation of grape juice, as hard, brown crust. It serves as the raw material for the manufacture of tartaric acid.

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[1]Fusel oil and other impurities contained in the raw spirits are very injurious to health.

10. Fermentation and Enzyme Action. It is a matter of common experience that vegetable and animal matter, particularly when moist, undergoes certain slow chemical changes by which the highly complex substances get gradually decomposed into simpler and still simpler compounds, until finally, in most cases, carbon dioxide, ammonia and water are produced. Souring of milk and kneaded flour, production of wine and vinegar, rotting of wood and vegetables, and putrefaction of meat, etc., are well-known examples of the changes of the above type which are collectively called **fermentation processes.**

Fermentation processes are brought about by certain living organisms called **ferments**. The action of ferments is due to the presence in their cells of complex nitrogenous substances called **enzymes**, which act catalytically.

The enzymes are extraordinarily *specific* in their action as catalysts. They are very sensitive to temperature changes, and are usually destroyed at about 70°C. The *optimum temperature*, *i e*, the temperature at which they are most active, lies between 25° and 36°C. Fermentation processes are exothermic in nature, the energy set free during the reaction is utilized by the ferment for its growth.

The simplest example of fermentation is that of sugar by yeast to form ethyl alcohol, C_2H_5OH. The yeast cells (Fig. 50) **contain** a number of enzymes, two of which, called **invertase** and **zymase**, are concerned in the alcoholic fermentation of sugars. The invertase first causes the hydrolytic decomposition of cane-sugar into glucose and fructose, which are then decomposed by zymase to form ethyl alcohol and carbon dioxide :—

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Another familiar example is the **lactic fermentation** of milk. When a small quantity of curd (*jag*) is added to warm milk, the sugar present in the milk is converted into lactic acid by a certain species of bacteria called lactic bacilli. The lactic acid causes the coagulation of the albumen present in the milk, producing curd. On keeping, the curd goes sour, as the lactic acid it contains is converted into butyric acid by the action of another ferment called **butyric bacillus.** The optimum temperature for the lactic fermentation is 34° to 35°C. ; hence the necessity of adding the ferment to warm milk.

A number of other examples of fermentation will be dealt with at their proper places.

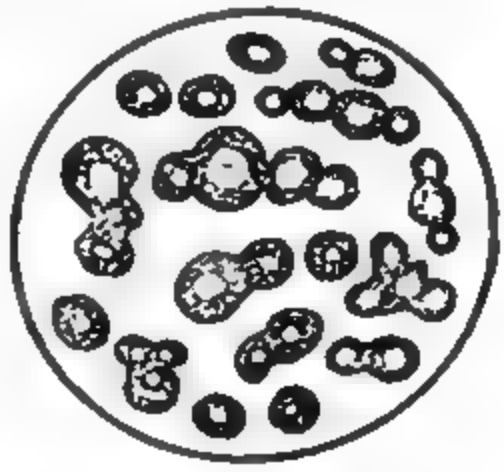


Fig. 4. Yeast cells (Highly magnified)

11. Theory of Fermentation. Pasteur, who carried out exhaustive researches on the fermentation of sugar, held the view that fermentation is a purely physiological action and is absolutely dependent upon the life processes of the yeast cells. Liebig, on the other hand, regarded the phenomenon as being of a purely chemical nature. Buchner carried out a series of experiments to settle this point He submitted yeast to strong pressure, thereby disrupting the cell walls and obtaining a juice. This was filtered, to free it completely from adhering cells. The "expressed

yeast juice" thus obtained was found to set up fermentation like the living yeast cells. He concluded that the yeast cells contained **enzymes,** or non-living, complex substances capable of bringing about fermentation. The yeast cells are, therefore, responsible for fermentation in only so far as they generate enzymes. Buchner also showed that the other fermentation processes, such as souring of milk, are not caused by the micro-organisms themselves but by the enzymes they contain.

12. Properties of Ethyl Alcohol. Ethyl Alcohol is a colourless, mobile liquid, having a pleasant, pungent odour. Absolute alcohol boils at 78·37°, and has a sp. gr. of 0·789 at 20°.

Ethyl alcohol forms a constant boiling mixture with water. This contains 96 per cent of alcohol, and boils at 78·3°C.

In dilute solution, ethyl alcohol has a specific intoxicating effect on the system. The use of spirits and liquors is based on this property. Ethyl alcohol is an excellent solvent for organic substances, such as resins and oils.

Ethyl alcohol burns with a pale blue, non-luminous flame. Its chemical reactions are analogous to those of methyl alcohol, and are as under :—

(1) With metallic sodium it forms **sodium ethoxide** :—

$$2C_2H_5OH + 2Na \rightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

(2) When treated with phosphorus pentachloride, PCl_5, or phosphorus trichloride, PCl_3, it gives **ethyl chloride** :—

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$3C_2H_5OH + 2PCl_3 \rightarrow 3C_2H_5Cl + P_2O_3 + 3HCl$$

(3) *Esterification.* Ethyl alcohol reacts with various acids, yielding esters. Thus, in the presence of zinc chloride, it reacts with hydrogen chloride, yielding *ethyl chloride*:—

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + H_2O$$

The zinc chloride serves to take up the water formed in the reaction. Similarly, with acetic acid it gives **ethyl acetate,** the reaction being carried out in the presence of concentrated sulphuric acid, which serves to "bind" the water formed in the reaction :—

$$C_2H_5OH + CH_3COOH \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

(4) *Reaction with Concentrated Sulphuric Acid.* When treated with concentrated sulphuric acid, ethyl alcohol yields three products according to experimental conditions :—

(i) When a mixture of equal volumes of the acid and the alcohol is heated at 100°, **ethyl hydrogen sulphate** is the main product (esterification) :

$$C_2H_5OH + H_2SO_4 \rightleftharpoons \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

(ii) If the alcohol be in excess and the temperature maintained at 140°, we get **diethyl ether,** $C_2H_5.O.C_2H_5$.

(iii) If, on the other hand, an excess of sulphuric acid is employed and the temperature kept at 160—165°, the alcohol is mainly converted

into *ethylene*. The reaction takes place in two stages :

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O$$
$$C_2H_5HSO_4 \rightarrow \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

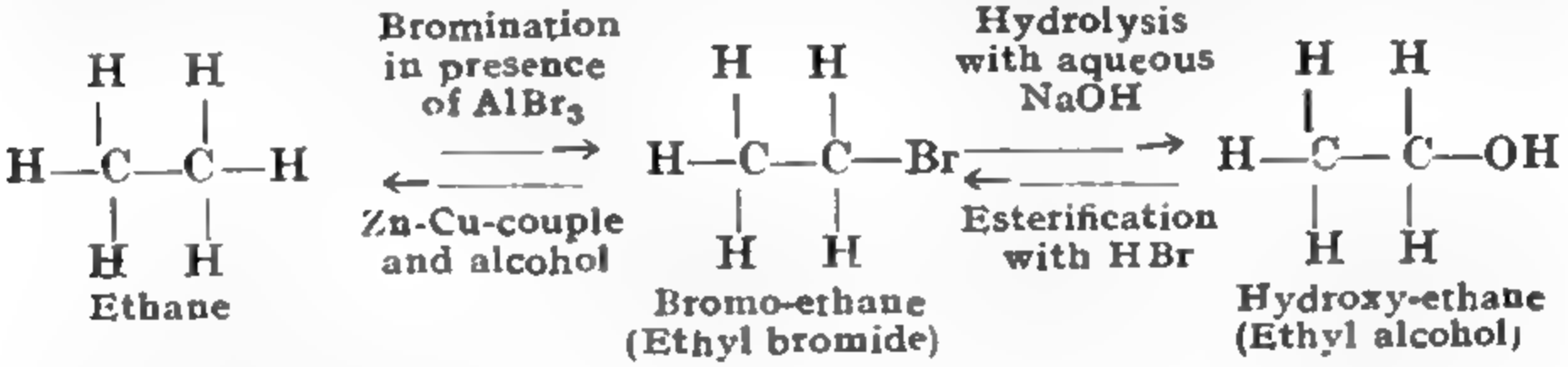
Methyl alcohol does *not* undergo this last rerction.

(5) *Oxidation*. Ethyl alcohol, like methyl alcohol, is a primary alcohol. When treated with potassium dichromate and sulphuric acid, it gets oxidized to **acetaldehyde** and then to **acetic acid** :—

$$CH_3.CH_2OH + O \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2O$$
$$CH_3.CHO + O \rightarrow \underset{\text{Acetic acid}}{CH_3.COOH}$$

Nitric acid oxidizes ethyl alcohol with explosive violence, producing, among other products, acetaldehyde, carbon dioxide and water.

13. Constitution. The structure of ethyl alcohol has already been discussed (*p.* 42). The structural relationship between ethane and ethyl alcohol is further confirmed by the following interconversions :



14. Detection. Ethyl alcohol can be readily detected as in the following experiments :—

Expt. 3. *Idoform Test.* Warm a small quantity of ethyl alcohol with a crystal of iodine, and then add a solution of potassium hydroxide, drop by drop, until the iodine colour just disappears. A yellow precipitate of iodoform, possessing a characteristic odour, will separate out either immediately or after some time. This test is given by several other compounds including acetone.

Expt. 4. *Ethyl Acetate Test.* Warm some alcohol with glacical acetic acid and concentrated sulphuric acid. A pleasant; fruity odour of ethyl acetate will be developed.

15. Estimation (Alcoholometry). The percentage of alcohol in a mixture of pure water and alcohol can be readily determined by noting the specific gravity of the mixture and then looking up the figure in a reference table. For instance, if the specific gravity is found to be 0·8605 at 15·5°, reference to the table would show that the sample contains 75 per cent of alcohol by weight. In case of beers, wines, and spirits the sugary and other extractive matters present influence the specific gravity to such an extent that a direct determination of specific gravity would be of no value. Hence, a measured quantity of the sample is submitted to distillation, until about one-half has passed over. The distillate, which contains practically the whole of the alcohol, is diluted with pure water to the original volume of the sample, and then the specific gravity is taken.

For revenue purposes, the standard is **proof spirit** which in Great Britain contains 49·3 per cent by weight, or 57·1 per cent by volume, of alcohol. Spirits are termed *under* or *over proof* according as they are weaker or stronger than proof spirit. Thus, 25° over proof means that

100 volumes of the sample contain as much of alcohol as 125 volumes of proof-spirit, whilst 25° under proof means that 100 volumes of the sample contains as much of alcohol as 75 volumes of proof spirit.

16. Alcoholic Beverages. Alcoholic beverages may be divided into two classes: (1) distilled beverages, and (2) undistilled beverages. Beer and wine are the chief undistilled beverages

Beer is made from barley, and is flavoured by the addition of hops. It contains from 3 to 6 per cent of alcohol and small quantities of dextrin, sugars, dissolved carbon dioxide, and other substances.

Wine is made from the juice of ripe grapes by means of a species of yeast which occur naturally in the bloom on the skin of the fruit itself. Natural wines contain from 8 to 15 per cent of alcohol and free sugar. Fementation automatically stops with the attainment of 15 per cent alcohol content, owing to the inability of yeast to grow in solution containing a higher proportion of alcohol.

In making **champaigne,** the grape juice is allowed to ferment in tightly closed bottles. The carbon dioxide, therefore, remains dissolved in the beverages, which consequently effervesces on the pressure being released.

Sweet **fortified wines,** such as port and sherry, contain about 20 per cent alcohol. They are made in the manner above indicated, and the alcohol content is then made up by the addition of pure alcohol. Some sugar and flavouring agents are also added to impart relish.

Another undistilled alcoholic beverage is cider, which is made from apple juice by the action of yeast and other organisms occurring naturally on the fruit. It contains from 4 to 8% of alcohol.

In making **distilled liquors,** the fermented liquid is subjected to distillation to increase the alcoholic content and to free the beverage from unpalatable constituents. They usually contain 40 to 50 per cent of alcohol.

Whisky is made from barley, **gin** from maize and **vodka** from rye. **Brandy** is made by distilling wine and **rum** by the distillation of fermented molasses.

17. Uses of Ethyl Alcohol. Ethyl alcohol is put to the following uses :—

(1) As already, mentioned it is a constituent of *alcoholic beverages* used so extensively.

(2) Alcohol is used as a *solvent* in the laboratory in making pharmaceutical tinctures, and in the preparation of varnishes and lacquers.

(3) It is also used as *fuel* in spirit lamps and spirit stoves. The use of alcohol as a **motor fuel** has attracted much attention. It is not sufficiently volatile to give proper starting in cold weather. This difficulty is overcome by using a mixture containing about 25 per cent of ether or petrol.

(4) Large quantities of alcohol are used in the production of numerous organic compounds, such as ether, chloroform, dyes, alkaloids, perfumes and collodion.

(5) Alcohol is also used as a *preservative* of biological specimens and as an *antiseptic* for the skin.

Note. For industrial purposes, such as the preparation of varnishes and lacquers and for use as a fuel, alcohol is employed in the form of

methylated spirit or *denatured alcohol.*

18. *n*-Propyl Alcohol. 1-*Propanol*, $CH_3.CH_2.CH_2OH$.

Occurrence and Isolation. This alcohol occurs in *fusel oil* (Sec. 9), from which it is obtained by fractionation.

Laboratory Preparation. *n*-Propyl alcohol may be prepared in the laboratary by reducing propionic aldehyde with sodium amalgam :

$$\underset{\text{n-Propionic aldehyde}}{CH_3.CH_2.CHO} + 2H \rightarrow \underset{\text{n-Propyl alcohol}}{CH_3.CH_2.CH_2OH}$$

Properties. *n*-Propyl alcohol is a colourless, mobile liquid, possessing a pleasant, spirituous odour, and boils at 97°, *i.e.*,19° higher than ethyl alcohol. It is completely miscible with water, but may be salted out by the addition of calcium chloride.

n-Propyl alcohol, being a *primary* alcohol, closely resembles ethyl alcohol in chemical behaviour. When submitted to oxidation, it yields propionic aldehyde and then propionic acid :

$$\underset{\text{n-Propyl alcohol}}{CH_3\ CH_2.CH_2OH} + O \rightarrow \underset{\text{Propionic aldehyde}}{CH_3.CH_2.CHO} + H_2O$$

$$CH_3.CH_2.CHO + O \rightarrow \underset{\text{Propionic acid}}{CH_3.CH_2.COOH}$$

Use. *n*-Propyl alcohol has been extensively used in organic synthesis, but is of no commercial importance.

19. Isopropyl Alcohol. 2-*Propanol*,$CH_3.CH(OH).CH_3$, or $(CH_3)_2$-CHOH.

Manufacture. Isopropyl alcohol is manufactured from propylene, obtained as a by-product in the cracking of heavy oils. The process consists in absorbing the hydrocarbon in sulphuric acid,

$$\underset{\text{Propylene}}{CH_3.CH = CH_2} + H_2SO_4 \rightarrow \underset{\text{Isopropyl hydrogen sulphate}}{(CH_3)_2CH(HSO_4)}$$

and decomposing the resulting ester by the addition of water,

$$(CH_3)_2CH(HSO_4) + H.OH \rightarrow \underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} + H_2SO_4.$$

The gas from the cracking stills, containing about 15% of the olefine hydrocarbons, is treated in towers with 87 per cent. sulphuric acid, which absorbs propylene and butylene but not ethylene. The solution is run into warm water, and after the separation of tarry matter, is subjected to fractionation.

Properties. Isopropyl alcohol boils at 81°, *i.e.*, only 3° higher than ethyl alcohol. Being a secondary alcohol, it yields a ketone on oxidation.

$$\underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CHOH} + O \rightarrow \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CO} + H_2O$$

When its vapour is passsed over hot, reduced copper at 300°, it gets decomposed into acetone and hydrogen.

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \rightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + H_2$$

On successive treatment with hydrogen iodide, silver nitrate and nitrous acid, it gives dark-blue **dimethyl pseudo-nitrol,** $(CH_3)_2C<\begin{matrix}NO_2\\NO\end{matrix}$.

Uses. Isopropyl alcohol is nowadays used in industries under the name of **petrohol.**[1] The name suggests the origin (petroleum) and nature (alcohol) of the substance. Large quantities are being used in the manufacture of **isopropyl acetate** which is employed as a solvent in lacquers. Petrohol is also used as a solvent in cosmetics and hair tonics and in the manufacture of acetone.

QUESTIONS

1. Into how many different classes are monohydric alcohols divided ? Give the behaviour of each class towards oxidizing agents.

2. Describe any experiment you have seen to show the products obtained by the destructive distillation of wood. *(Unit., Prov., Inter., 1923)*

3. Describe a method for the manufacture of methyl alcohol. *(Punjab, Inter., 1932)*

4. Give the chief chemical properties of methyl alcohol. How may it be distinguished from ethyl alcohol ? To what different uses is methyl alcohol put ?

5. What is the action of phosphorus trichloride on alcohol and acids ? *(Unit., Prov., Inter. 1921)*

6. How is ethyl alcohol prepared on a large scale ? Mention the varouis raw materials used and briefly state the changes involved in their conversion into alcohol. *(Unit., Prov., Inter., 1931)*

7. Explain clearly and illustrate what you understand by *Fermentation.* *(Unit., Prov., Inter., 1922)*

8. What products are obtained by the oxidation of ethyl alcohol ? *(Unit., Prov., Inter., 1920)*

9. What is the action of sulphuric acid on ethyl alcohol ? Describe briefly the conditions under which the various products are formed. *(Ajmer. Inter., 1930)*

10. Write a note on *Alcholometry.* *(Ajmer. Inter., 1934)*

11. Starting from methyl alcohol, explain, illustrating your answer by equations, how ethyl alchol can be produced. *(Unit., Prov., Inter., 1926)*

12. Describe the synthesis and chief properties of normal propyl alcohol. In what important respects does it differ from isopropyl alcohol ?

13. Describe the manufacture, charcteristic reactions and uses of isopropyl alcohol.

14. Starting from a starchy meterial, how would you obtain a sample of absolute alcohol ? Describe all the stages involved, and show how you can test and estimate alcohol in a syrup.

15. Describe the distillation of wood and state the products obtained. How are the various products separated from one another ? *(Unit., Prov., Inter., 1942)*

CHAPTER 11

ETHERS

1. General. The ethers are isomeric with alcohols, and possess the same general **molecular formula**, *viz.*, $C_nH_{2n+2}O$. Structurally, they are regarded as the anhydrides of alcohols in the same sense as the metallic oxides are the anhydrides of metallic hydroxides.

Ethyl alcohol, C_2H_5OH — Ethyl ether, $C_2H_5.O.C_2H_5$
Sodium hydroxide, NaOH — Sodium oxide, Na_2O.

An ether is said to be **simple** of **mixed**, according as the two alkyl groups linked to the oxygen atom are identical or different. Thus, diethyl ether, $C_2H_5.O.C_2H_5$, is a simple ether, while methyl ethyl ether, $CH_3.O.C_2H_5$, is a mixed ether. Ethers exhibit **metamerism** (Chap. 6, Sec. 5)

2. General Methods of Formation. Ether may be prepared by the following general methods :—

(1) From Alcohols :

(*i*) *By Heating with Concentrated Sulphuric Acid.* This reaction is of great practical importance, and will be described in detail in the case of ethyl ether.

(*ii*) *By Catalytic Dehydration.* In this method, the alcohol vapour is passed over precipitated alumina heated at 240° to 260° :

$$2C_2H_5OH \rightarrow C_2H_5.O.C_2H_5 + H_2O$$

(2) From Alkyl Halides :

(*i*) *By Heating with Sodium Alkoxides* (**Willamson's Synthesis**) : *e.g.*,

$$C_2H_5\ I + Na\ O.C_2H_5 \longrightarrow C_2H_5.O.C_2H_5 + NaI$$

Sodium ethoxide — Ethyl ether

This method is of great theoretical interest, since it shows very clearly the structure of ethers Moreover, it affords a simple method for synthesizing any desired ether, simple or mixed Thus, methyl ethyl ether may be obtained by heating a mixture of methyl iodide and sodium ethoxide or of ethyl iodide and sodium methoxide

(*ii*) *By Heating with Silver Oxide* ; *e.g* ,

$$2C_2H_5I + Ag_2O \rightarrow C_2H_5\ O.C_2H_5 + 2AgI.$$

3. Properties of Ethers (*a*) ***Physical.*** With the exception of dimethyl ether, which is gaseous at ordinary temperatures, the aliphatic ethers are colourless, mobile, and volatile liquids, having a pleasant odour. They are highly inflammable, and are lighter than water. Ethers dissolve in water to a very limited extent.

(*b*) ***Reactions.*** Chemically, ethers are far more inactive than alcohols, and are stable towards metallic sodium, alkalies, and phosphorus pentachloride in the cold. The following reactions that the ethers undergo prove their constitution as anhydrides of alcohols :—

(1) *Hydrolysis.* Superheated water containing a little sulphuric acid slowly decomposes ethers into alchols :

$$C_2H_5.O.C_2H_5 + H.OH \rightarrow 2C_2H_5.OH$$

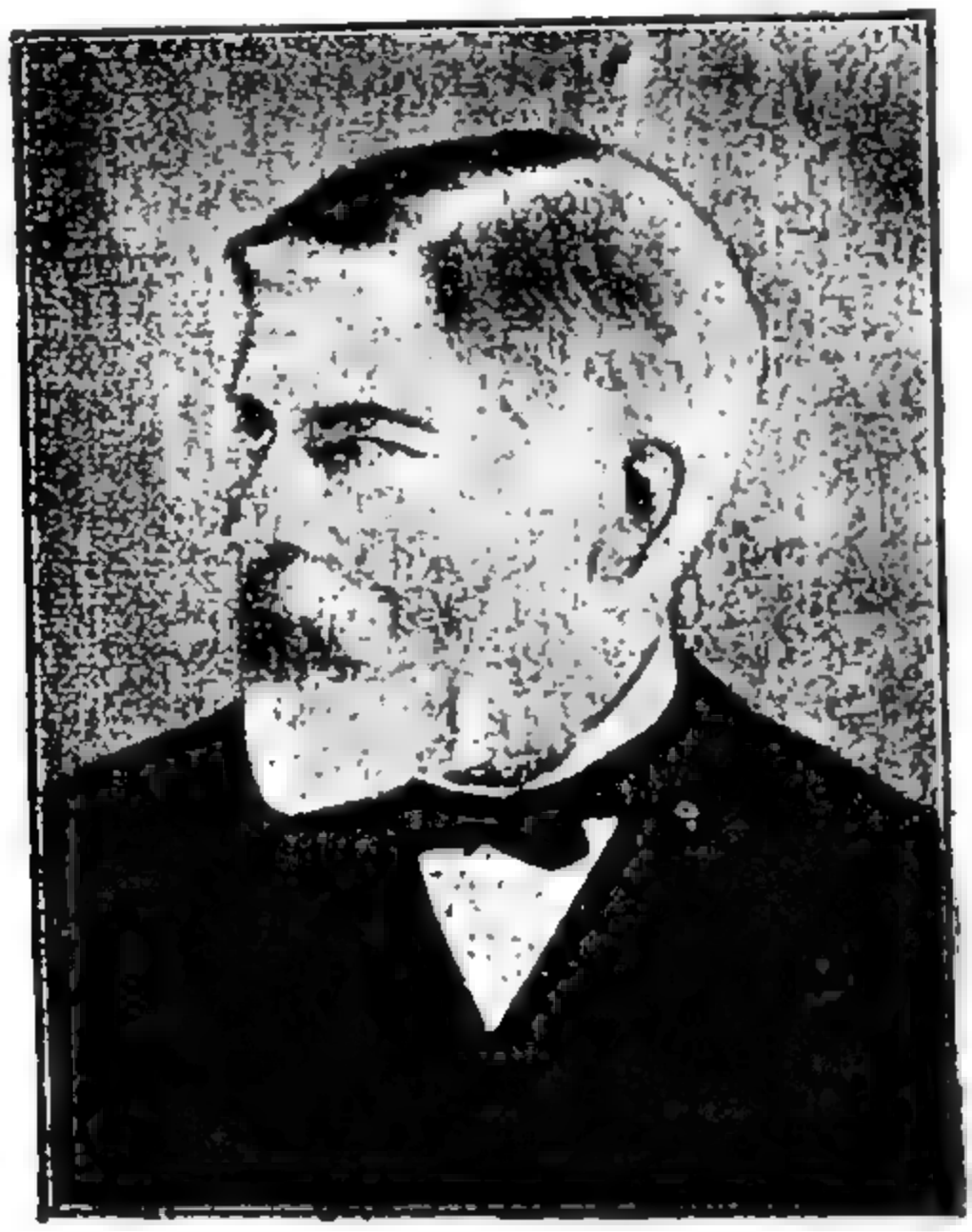
(2) *Action of Concentrated Acids.* When heated with concentrated acids, ethers yield esters :

$$C_2H_5.O.C_2H_5 + H_2SO_4 \rightleftharpoons C_2H_5.HSO_4 + C_2H_5OH$$
$$C_2H_5.O.C_2H_5 + HI \rightarrow C_2H_5I + C_2H_5OH$$

The excess of the acid may, of course, react with the alcohol produced, yielding a further quantity of the ester.

(3) *Action of Phosphorus Pentachloride.* When *heated* with phosphorus pentachloride, the ethers are decomposed, yielding alkyl chlorides:

$$C_2H_5.O.C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3$$



ALEXANDER WILLIAM WILLIAMSON
(1824—1904)

was an English chemist, who investigated the *etherification process* and established the real nature of ether and its genetic relation to alcohol.

Constitution. The constitution of ethers as alkyl oxides follows from Williamson's synthesis, and is fully supported by their reactions.

4. Diethyl Ether, *Ethyl Ether*, or simply *Ether* $C_2H_5.O.C_2H_5$. This is the most important member of the homologous series of ethers.

Preparation. (1) Ether is prepared both technically and in the laboratory by heating a mixture of ethyl alcohol and concentrated sulphuric acid at 140°. The reaction has been shown to occur in two stages:—

$$(i)\quad \underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \rightleftharpoons \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5.HSO_4} + H_2O$$

$$(ii)\quad C_2H_5.HSO_4 + C_2H_5OH \rightarrow \underset{\text{Ethyl ether}}{C_2H_5.O.C_2H_5} + H_2SO_4$$

The ethyl hydrogen sulphate, produced in the first stage of the reaction, reacts with more of the alcohol producing ether and regenerating sulphuric acid. The latter then acts once again with a further quantity of alcohol, producing more of ethyl hydrogen sulphate and ether. The process is therfore, *continuous*, and theoretically a small amount of sulphuric acid will etherify an unlimited quantity of alcohol. Actually

however, side reactions occur and the acid is gradually destroyed, owing to its reduction to sulphur dioxide.

Expt. 1. The apparatus employed for the preparation is shown in Fig. 1. A half-litre distillation flask is fitted with a dropping funnel and a thermometer. Its side tube is attached to a long condenser, the lower end of which is fitted into the neck of a second distillation flask to act as the receiver. A long rubber tube is attached to the side tube of the receiver to carry off the ether vapour into the sink. This arrangement prevents the ether vapour from catching fire.

50 c.c. of concentrated sulphuric acid are gradually added, with constant shaking, to 100 c.c. of alcohol contained in the distillation flask. The latter is then heated on a sand bath, until the temperature rises to about 140°, when ether begins to distil over. Alcohol is run in from the dropping funnel at nearly the same rate as that of the distillation, the temperature being kept at 140°

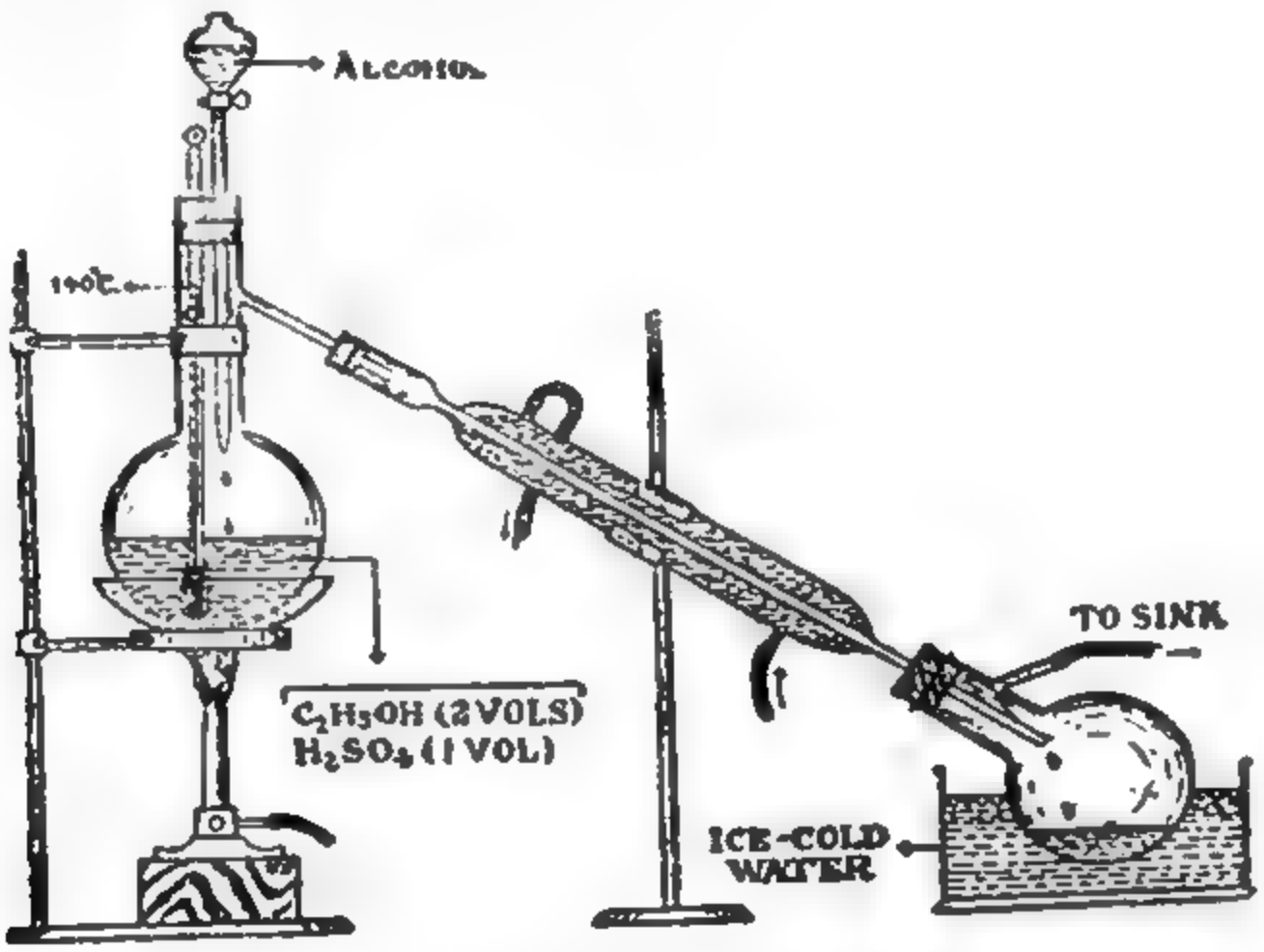


Fig. 1. Preparation of Ethyl Ether in the Laboratory.

The distillate contains alcohol, water, and sulphur dioxide, in addition to ether. It is purified by shaking it in a separating funnel with a solution of sodium hydroxide, to remove sulphur dioxide. The upper ethereal layer is separated and dried over anhydrous calcium chloride. It is then redistilled from a water-bath, when pure ether passes over at 34° to 35° C.

(2) Williamson's Synthesis. Ether can be obtained by heating a mixture of ethyl iodide and sodium ethoxide :

$$C_2H_5\,I + \overline{Na}\,O.C_2H_5 \rightarrow C_2H_5.O.C_2H_5 + NaI$$

This reaction was discovered by Williamson, and is of great importance, since it proves the structural relationship of ether and alcohol.

(3) Ether may also be synthesised by heating ethyl iodide with silver oxide :—

$$2C_2H_5I + Ag_2O \rightarrow C_2H_5.O.C_2H_5 + 2AgI$$

Manufacture. As already stated, ethyl ether is manufactured by the etherification of ethyl alcohol. Equimolecular proportions of the alcohol and concentrated sulphuric acid are introduced in a vessel provided with a closed coil through which superheated steam can be circulated (Fig. 2). The mixture is heated to about 140°C by means of superheated steam, and more alcohol is added at about the same rate at which ether distils over. The distillate is washed with a solution of sodium carbonate, dried with anhydrous calcium chloride, and redistilled.

Physical Properties: Ethyl ether is a colourless, mobile and highly volatile liquid, boiling at 35·5° It is only slightly soluble in water (1 vol. in 11 vols. at 25°).

Reactions: Ether is far more stable than alcohol, and is not acted upon by metallic sodium, alkalies, and phosphorus pentachloride in the cold. The following are its chief reactions :

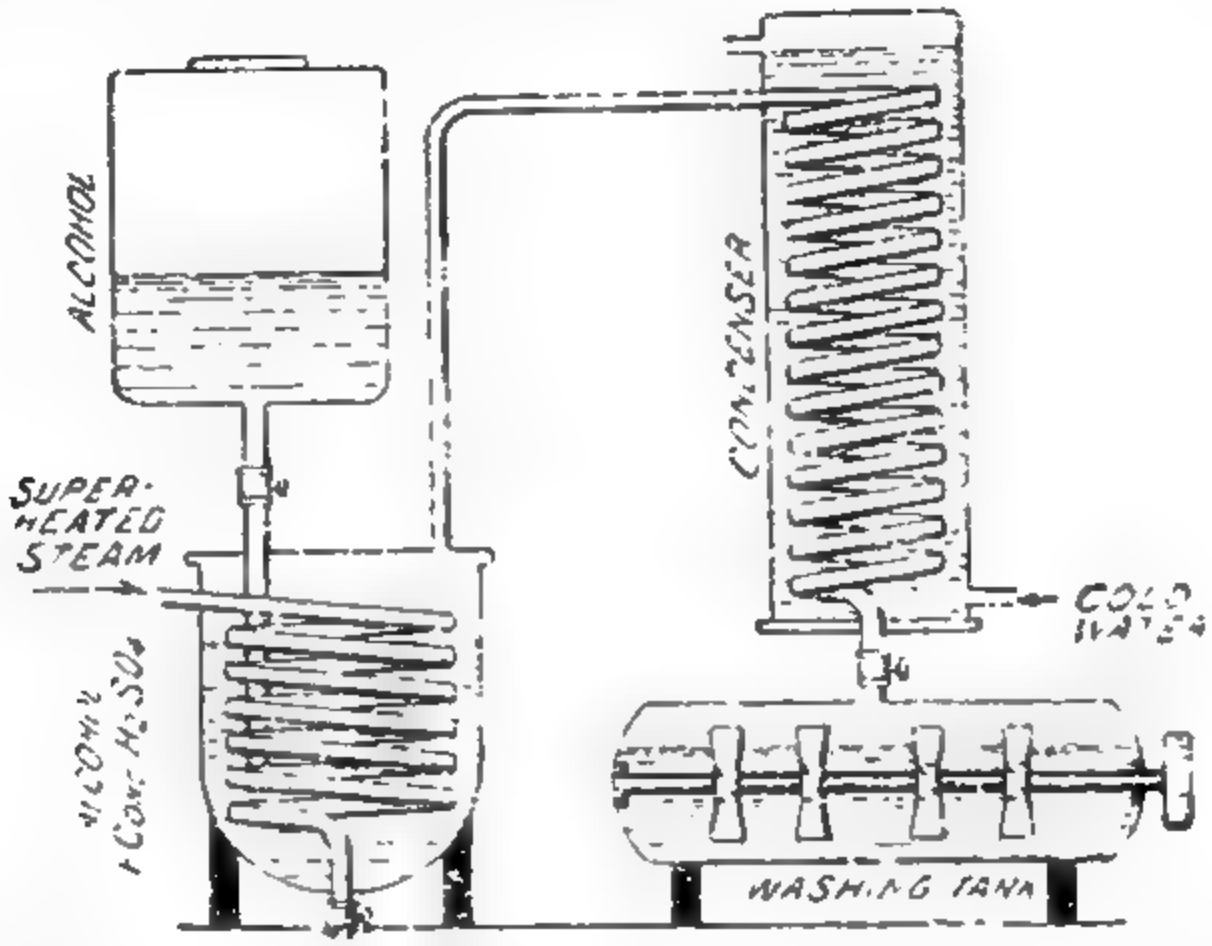


Fig. 2. Continuous Etherification Process for the Manufacture of Ether.

(1) *Hydrolysis.* Superheated water, containing a little sulphuric acid, slowly decomposes ether into ethyl alcohol :

$$C_2H_5.O.C_2H_5 + H.OH \rightarrow 2C_2H_5.OH$$

(2) *Action of Concentrated Acids.* When heated with concentrated acids, ether yields esters :

$$C_2H_5.O.C_2H_5 + H_2SO_4 \rightleftharpoons \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5.HSO_4} + C_2H_5OH$$

$$C_2H_5.O.C_2H_5 + HI \rightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + C_2H_5OH$$

The excess of the acid may, of course, react with the alcohol produced, yielding a further quantity of the ester.

(3) *Action of Phosphorus Pentachloride* :

$$C_2H_5.O.C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3$$

Uses. Ether is put to the following uses :—

(1) As a solvent for many organic substances ;

(2) As an anaesthetic in surgery.

Structure. Williamson's synthesis of ether, given on p. 110, proves that this compound has the structural formula $C_2H_5.O.C_2H_5$. This view of the structure of ether is fully supported by its chemical reactions.

QUESTIONS

1. Give the methods of preparation of ethers. Why do we represent diethyl ether as $C_2H_5.O.C_2H_5$? (*Punjab, Inter., 1929*)

2. Describe, with all essential details, the preparation of ethyl ether. How would you purify it and make it anhydrous ? Give its structural formula. (*Unit. Prov., 1932*)

3. Give an account of the physical and chemical properties of ordinary ether. How may it be synthesised from elements? *(Punjab, Inter., 1947)*

4. Write the constitutional formulae of the two isomers having the molecular formula C_2H_6O. *(Unit. Prov., Inter., 1924)*

5. Two organic compounds containing carbon, hydrogen and oxygen gave on analysis the same results, *viz* :—

0·1245 gm. gave on combustion 0·1471 gm. of water and 0·2374 gm. of CO_2. Each of them was found to have 23 as its vapour density. What constitutional formula would you assign to each? By what reactions would you prove the correctness of the formulae? *(Bombay, Inter., 1925)*

Ans C_2H_5OH ; $CH_3.O.CH_3$.

6. Describe the preparation of ethyl ether and draw a sketch of the apparatus you could use. Describe the physical and chemical properties of ether. How would you test for the presence of moisture in a sample of ethyl ether? *(Unit. Prov. Inter., 1941)*

CHAPTER 12

ALDEHYDES AND KETONES

1. General. The aldehydes and ketones derived from the paraffin hydrocarbons constitute two *isomeric* series of carbon compounds, each posses-ing the **general formula** $C_nH_{2n}O$ Both the classes contain the divalent **carbonyl group** $>CO$, which in the case of aldehydes is linked on the one hand to an alkyl radical and on the other to hydrogen, while in ketones it is linked, to two alkyl groups. The aldehydes therefore, contain the **aldehyde group,** $-C\leqslant^{H}_{O}$. If the two alkyl groups in a ketone be identical, the ketone is termed a **simple ketone,** and if they are different, it is called a **mixed ketone** (compare ethers).

$\begin{matrix}R\\H\end{matrix}>C=O$	$\begin{matrix}R\\R\end{matrix}>C=O$	$\begin{matrix}R\\R'\end{matrix}>C=O$
Aldehyde	Simple ketone	Mixed ketone

Ketones, like ethers, exhibit metamerism (Chap 6, Sec. 5).

Aldehydes and ketones are oxidation products of primary and secondary alcohols respectively, being derived from these by the removal of two hydrogen atoms. The change may be supposed to take place in two stages: In the first instance, an oxygen atom is added, with the production of a compound having two hydroxyls linked to the same carbon atom. This compound, since it is unstable, immediately loses a molecule of water, yielding an aldehyde or a ketone :

$R.CH_2.OH$	$\xrightarrow{-O}$	$R.CH(OH)_2$	$\xrightarrow{-H_2O}$	$R.C\leqslant^{H}_{O}$
Primary alcohol		Unstable intermediate product		Aldehyde

$\begin{matrix}R\\R'\end{matrix}>CHOH$	$\xrightarrow{-O}$	$\begin{matrix}R\\R'\end{matrix}>C(OH)_2$	$\xrightarrow{-H_2O}$	$\begin{matrix}R\\R'\end{matrix}>C\quad O$
Secondary alcohol		Unstable intermediate product		Ketone

Aldehydes are usually named after the acid they give rise to on oxidation, and ketones after the alkyl groups that they contain. Simple ketones are also named after the acid from which they may be obtained by the action of heat on its calcium salt. The Geneva names of aldehydes and ketones are derived from those of parent hydrocarbons by replacing the terminal *-e* by *-al* for aldehydes and by *-one* tor ketones. The following few examples illustrate the nomenclature adopted :

$H\,CHO$	$CH_3.CHO$	$CH_3.CO.CH_3$
Formaldehyde or Methanal	Acetaldehyde or Ethanal	Dimethyl ketone Acetone, or Propanone

Acetaldehyde is a typical aldehyde and acetone a typical ketone. Formaldehyde differs from other aldehydes in certain important respects (*see* Sec. 8, C).

2. General Methods of Formation. Aldehydes and ketones may be obtained by the following methods :—

(1) FROM PRIMARY AND SECONDARY ALCOHOLS :—

(i) *By Oxidation.* Aldehydes are obtained by the oxidation of primary alcoho's and ketones of the secondary alcohols ; *e.g.*

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + O \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2O$$

$$\underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CH.OH} + O \rightarrow \underset{\text{acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CO} + H_2O$$

The oxidation is generally effected by means of potassium dichromate in the presence of sulphuric acid.

(*ii*) *By Catalytic Decomposition.* When the vapours of primary and secondary alcohols are passed over finely divided copper (obtained by reducing CuO) heated at 300°C., dehydrogenation occurs with the production of aldehydes and ketones respectively : *e.g.*,

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \rightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + H_2$$

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CH.OH} \rightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + H_2$$

Note From methods of preparation (*i*) and (*ii*) it can be seen that aldehydes are derived from the corresponding alcohols by the loss of two atoms of hydrogen hence the term *aldehyde* which is an abbreviation of *alcohol dehydrogenatum* (*i.e.*, alcohol from which hydrogen has been removed)

(2) FROM CARBOXYLIC ACIDS :—

(*i*) *By Dry Distillation of Calcium Salts.* When the calcium salt of a fatty acid (other than formic) is subjected to dry-distillation, we get a simple ketone : *e.g.*,

$$\underset{\text{Calcium acetate}}{\begin{matrix}CH_3COO\\CH_3COO\end{matrix}>Ca} \rightarrow \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CO} + CaCO_3$$

Calcium formate, when heated alone, yields formaldehyde.

$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \rightarrow \underset{\text{Formaldehyde}}{H.CHO} + CaCO_3.$$

When a mixture of this salt with the calcium salt of some other fatty acid is used, the product is an aldehyde. Thus,

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} \rightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3.$$

If a mixture of calcium salts of fatty acids (excluding formic) is employed a mixed ketone is produced : *e.g.*,

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium propionate}}{(C_2H_5COO)_2Ca} \rightarrow \underset{\text{Methyl-ethyl ketone}}{2CH_3.CO.C_2H_5} + 2CaCO_3.$$

(*ii*) *By Catalytic Decomposition.* When the vapour of an aliphatic acid is passed over precipitated aluminium oxide at 400°C. a simple ketone is obtained :

$$2CH_3COOH \rightarrow CH_3.CO.CH_3 + H_2O + CO_2.$$

Similarly, when a mixture of formic acid and another fatty acid, in vaprous state, is passed over titanium oxide at 300°C, we get an aldehyde, formic acid acting as a reducing agent :

$$\underset{\text{Acetic acid}}{CH_3COOH} + H.COOH \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2O + CO_2.$$

(*iii*) *By Catalytic Reduction of Acid Chlorides.* **(Rosenmund's method).** When an acid chloride is reduced by means of hydrogen in the presence of platinized barium sulphate (*i.e.*, finely divided platinum precipitated on $BaSO_4$), an aldehyde is formed : *e.g.*,

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \rightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

(3) From Dihalides. When a dihalogen derivative of a hydrocarbon, containing both the halogen atoms linked to the *same* carbon atom, is hydrolysed by means of superheated water,[1] or by boiling with water and plumbous oxide, we get an aldehyde or a ketone, the former, if the two halogen atoms be linked to a *terminal* carbon atom, and the latter, if they be carried by an *intermediate* carbon atom. The reaction is supposed to occur in two stages : The dihydroxy derivative, which is first formed, loses the elements of water yielding an aldehyde or a ketone.

$$\underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} \xrightarrow{H\,OH} \underset{\substack{\text{Unstable}\\ \text{dihydroxy compound}}}{CH_3.CH(OH)_2} \xrightarrow{-H\;O} \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

$$\underset{\substack{2:2\text{--Dichloropropane}}}{CH_3.CCl_2.CH_3} \xrightarrow{H.OH} \underset{\substack{\text{Unstable}\\ \text{dihydroxy compound}}}{CH_3.C(OH)_2.CH_3} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

Note. Except in rare cases, a compound containing two hydroxyl groups linked to the *same* carbon atom is unstable, and loses a molecule of water to give the corresponding anhydride.

3. Physical Properties of Aldehydes and Ketones. Excluding formaldehyde, which, at ordinary temperatures, exists as a gas, the aldehydes and ketones up to about C_{11} are colourless, mobile liquids, the higher members being solids.

The boiling point of some of the more important aldehydes and ketones are given in the following table :—

Aldehyde	B.P.	Ketone	B.P.
Formaldehyde, H.CHO	−21°	Acetone, $CH_3.CO.CH_3$	56°
Acetaldehyde, $CH_3.CHO$	+21	Methylethyl ketone $CH_3.CO.C_2H_5$	81
Propionaldehyde, $C_2H_5.CHO$	49	Diethyl ketone, $C_2H_5.CO.C_2H_5$	103

As a rule, aldehydes possess an unpleasant, pungent odour, while ketones have a pleasant smell. The first two or three members of both homologous series are readily soluble in water, but, as the molecular weight rises, the solubility rapidly decreases, the higher members being practically insoluble in water. They are, however, readily soluble in alcohol and ether. The specific gravity and the boiling point continuously rise with the increase in the number of carbon atoms.

4. Reactions Common to Aldehydes and Ketones. Since both the aldehydes and the ketones contain the carbonyl group, >CO, they resemble each other in most of their chemical properties. The aldehydes, however, are more reactive than the ketones, this being due to the presence of the hydrogen atom linked to the carbonyl group.

The **reactions of the >CO group** may be divided into two classes :

(1) **Addition Reactions.** Aldehydes and ketones form addition compounds with certain substances containing hydrogen, the addition always occurring in such a manner that the hydrogen goes to the carbonylic oxygen, forming a hydroxyl group.

(1) Alkali *cannot* be used for effecting hydrolysis in this case as it would resinify the resulting aldehyde.

(*i*) *Addition of Hydrogen.* When treated with nascent hydrogen (sodium amalgam and dilute sulphuric acid), aldehydes yield primary alcohols, and ketones secondary alcohols :—

$$CH_3.C\leqslant^{H}_{O} + 2H \rightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

Acetaldehyde

$$CH_3.CO.CH_3 + 2H \rightarrow \underset{\text{Isopropyl alcohol}}{CH_3CH(OH).CH_3}$$

Acetone

(*ii*) *Addition of Hydrogen Cyanide.* When an aldehyde or a ketone is treated with hydrogen cyanide, we get a **cyanohydrin** :

$$CH_3.C\leqslant^{H}_{O} + HCN \rightarrow CH_3.C\begin{cases}H\\OH\\CN\end{cases}$$

Acetaldehyde — Acetaldehyde cyanhydrin

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!=\!O + HCN \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CN\end{matrix}$$

Acetone — Acetone cyanhydrin

(*iii*) *Addition of Sodium Bisulphite.* On shaking aldehydes and ketones with very concentrated solutions of sodium bisulphite, crystalline addition compounds are obtained :

$$CH_3C\leqslant^{H}_{O} + NaSHO_3 \rightarrow CH_3C\begin{cases}H\\OH\\OSO_2Na\end{cases}$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!=\!O + NaHSO_3 \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\OSO_2Na\end{matrix}$$

These so-called **bisulphite compounds** are readily soluble in water, but are insoluble in very concentrated solutions of sodium bisulphite. On warming them with dilute acids or alkalies, the aldehyde or ketone is again set free. Hence the formation of these compounds is employed for the **purification and separation of aldehydes and ketones.**

(2) **Substitution of Carbonylic Oxygen.** Aldehydes and ketones react with certain reagents, exchanging the oxygen of the carbonyl group for other atoms or groups

(*i*) *Hydroxylamine*, NH_2OH, reacts with aldehydes and ketones to form crystalline compounds called **oximes**, water being eliminated :

$$RCH=O + H_2NOH \rightarrow \underset{\text{Aldoxime}}{R.CH=NOH} + H_2O$$

$$\begin{matrix}R\\R'\end{matrix}\!>\!C\!=\!O + H_2NOH \rightarrow \underset{\text{Ketoxime}}{\begin{matrix}R\\R'\end{matrix}\!>\!C\!=\!NOH} + H_2O$$

Oximes, like the bisulphite compounds, are employed for the isolation and identification of aldehydes and ketones. When heated with hydrochloric acid, they regenerate the original aldehyde or ketone.

(*ii*) *Phenylhydrazine*, $H_2N.NHC_6H_5$, reacts with aldehydes and ketones in an exactly similar manner as hydroxylamine, yielding products called **phenylhydrazones :**

$$CH_3CH=O + H_2N.NH.C_6H_5 \rightarrow \underset{\text{Acetaldehyde phenylhydrazone}}{CH_3.CH=N.NHC_6H_5} + H_2O$$

Acetaldehyde

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!=\!O + H_2N.NH.C_6H_5 \rightarrow \underset{\text{Acetone phenylhydrazone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!=\!N.NH.C_6H_5} + H_2O$$

Acetone

The formation of phenylhydrazones is also utilized for the isolation

and identification of aldehydes and ketones, since they are very readily crystallizable, and, on being heated with hydrochloric acid, take up the elements of water, regenerating the original aldehyde or ketone.

(*iii*) *Action of Phosphorus Pentachloride.* When an aldehyde or a ketone is treated with phosphorus pentachloride, the oxygen atom of the >CO group gets replaced by two chlorine atoms :

$$CH_3.CHO + PCl_5 \rightarrow \underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} + POCl_3$$

$$CH_3.CO.CH_3 + PCl_5 \rightarrow \underset{\text{2:2 Dichloro-propane}}{CH_3.CCl_2.CH_3} + POCl_3$$

5. Reactions in which Aldehydes differ from Ketones :

(1) *Reducing Properties.* Because of the presence of the hydrogen atom directly united to the carbonyl group (termed the **aldehydic hydrogen atom**), aldehydes possess active reducing properties, giving carboxylic acidscontaining the *same* number of carbon atoms as the aldehydes. Thus,

$$CH_3C\leqslant^{H}_{O} + O \rightarrow \underset{\text{Acetic acid}}{CH_3C\leqslant^{OH}_{O}}$$

Acetaldehyde

The aldehydes reduce ammoniacal silver nitrate solution and Fehling's solution. Tollens' reagent produces with a dilute solution of an aldehyde a **silver mirror** in the cold. (*See* Expts. 1,2 and 3.)

Ketones, since they do not contain a readily oxidizable hydrogen atom, possess no reducing properties whatever. When treated with energetic oxidizing agents, their molecules break up, yielding acids with *smaller* number of carbon atoms. Thus, acetone gives acetic and carbonic acids :—

$$CH_3.CO.CH_3 + 4O \rightarrow CH_3COOH + H_2O + CO_2$$

Expt. 1. *Silver Mirror Test.* To a solution of silver nitrate add, drop by drop, a very dilute solution of ammonia, until the precipitate of silver hydroxide, first formed, *just* redissolves. Add a few drops of acetaldehyde, and place the test-tube in boiling-hot water ; bright silver mirror will be formed on the inside of the test-tube.

Expt. 2. *Silver Mirror Test.* Add a dilute solution of acetaldehyde to a few ml. of Tollens' reagent (prepared by mixing together equal volumes of 10 per cent aqueous solutions of silver nitrate and sodium hydroxide and adding just enough ammonia to dissolve the silver hydroxide). A silver mirror is deposited in the cold.

Expt. 3. *Reduction of Fehling's Solution.* Add a few drops of acetaldehyde to some Fehling's solution (a solution of cupric sulphate containing Rochelle salt and caustic soda), and warm the mixture. A red precipitate of cuprous oxide will be formed.

(2) *Polymerization.* Aldehydes possess a remarkable power to polymerize. The polimerization products of formaldehyde and those of acetaldehyde are discussed under these aldehydes.

Ketones do *not* polymerize ; they undergo condensation with elimination of water.

(3) *Schiff's Reaction.* Aldehydes differ from ketones in giving the following reaction.

Expt. 4. Bubble sulphur dioxide through a dilute, aqueous solution of magenta (fuchsine or rosaniline) until decolorized. Add to this reagent a few drops of acetaldehyde ; a violet coloration is developed.

(4) *Resinification by Alkalies.* When aldehydes are warmed with a concentrated alkali solution, they get polymerized, yielding brown coloured, resinous products called **aldehyde resins.**

Expt. 5. *Resinification Test.* Warm some acetaldehyde with sodium hydroxide solution. A brownish yellow coloration is produced.

(5) *Formation of Aldehyde-ammonias.* Acetaldehyde combines with anhydrous ammonia, forming a crystalline compound, called **acetaldehyde ammonia** :

$$CH_3.CHO + NH_3 \rightarrow C_2H_4ONH_3,$$

whose molecular formula, at the ordinary temperature, has been found to be $(C_2H_4ONH_3)_3$. Some other aldehydes also form aldehyde-ammonias, but the reaction is not a general one. Thus, formaldehyde behaves differently (*p.* 120).

The aldehyde-ammonia formation is utilized in the **purification of aldehydes**. The crystalline precipitate is filtered off, and warmed with dilute sulphuric acid, when aldehyde is regenerated.

Ketones, as a rule, do not give addition compounds with ammonia ; they behave differently and form peculiar condensation products.

(6) *Formation of Acetals.* When heated with excess of an alcohol, particularly in the presence of dehydrating agents, aldehydes yield a kind of double ethers, known as **acetals** :

$$CH_3.CH{<}\begin{matrix}O\\O\end{matrix} + \begin{matrix}H\\H\end{matrix}{>}O.C_2H_5 \rightarrow CH_3.CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + H_2O$$

Acetaldehyde — Ethyl alcohol (2 molecules) — Acetal

Acetals are colourless liquids with an aromatic odour.

6. Tests of Aldehydes. The following reactions are utilized as tests for *aldehydes* :—

(1) *Silver Mirror Test.* See Expts. 1 and 2, *p.* 117.
(2) *Reduction of Fehling's solution.* See Expt. 3, *p.* 117.
(3) *Schiff's Test.* See Expt. 4, *p.* 117.
(4) *Resinification by Alkalies.* See Expt. 5.

7. Formaldehyde. *Methanal*, $H.CHO$.

Preparation. (1) *Oxidation of Methyl Alcohol.* Formaldehyde is generally prepared by the oxidation of methyl alcohol. A mixture

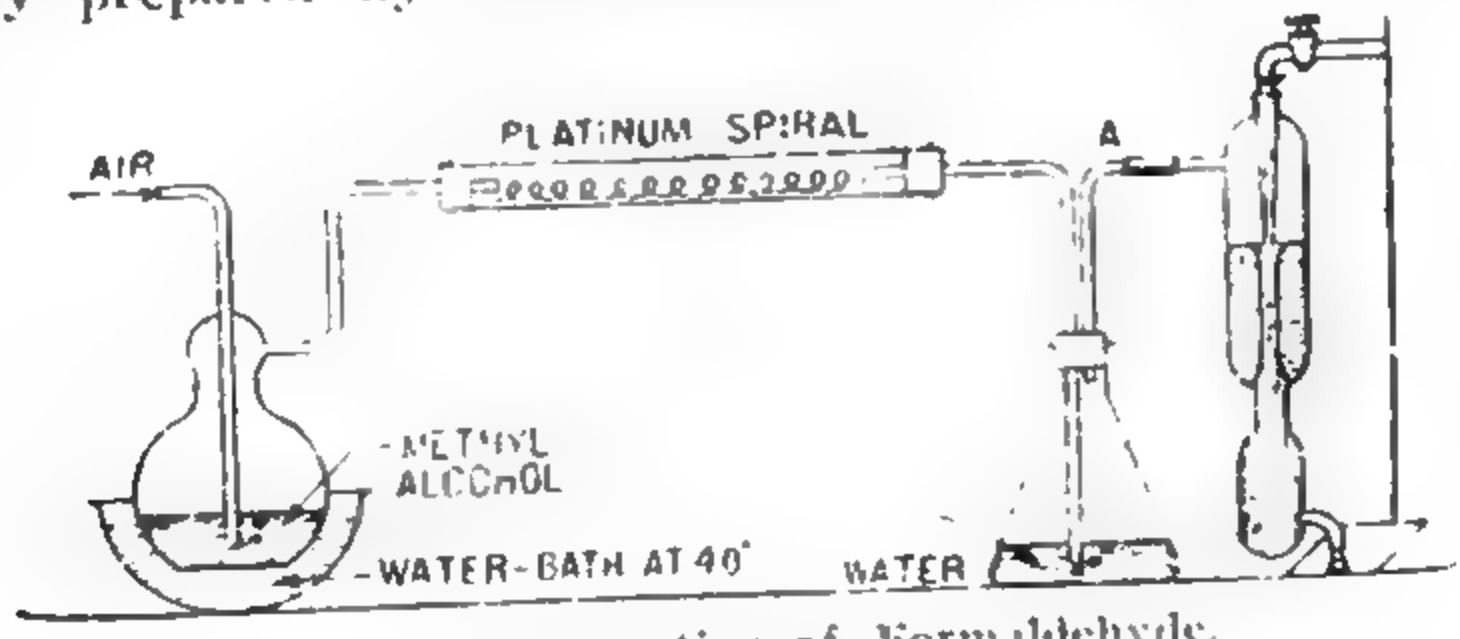


Fig 1. Preparation of Formaldehyde.

of the vapour of methyl alcohol and air is passed over a heated spiral of platinum or copper (Fig. 1).

$$\underset{\text{Methyl alcohol}}{CH_3OH} + O \rightarrow \underset{\text{Formaldehyde}}{H.CHO} + H_2O$$

or,

$$2CH_3OH + O_2 \rightarrow 2H.CHO + 2H_2O.$$

The heat of reaction raises the temperature of the spiral to redness,

and keeps it at that point, provided the rate at which the gaseous mixture is passed is sufficiently quick. The resulting formaldehyde (which is a gas at the ordinary temperature) is absorbed in water.

Expt. 6. *Preparation of Formaldehyde.* Set up the apparatus as shown in Fig. 1 Heat methyl alcohol by means of hot water at 40° placed in a dish, and pass a rapid current of air by attaching the bent tube, *A*, to a water-pump. Heat the hard glass tube containing the platinum spiral, until the latter is red-hot. Formaldehyde is obtained as an aqueous solution.

(2) *By Catalytic Decomposition of Methyl Alcohol.* When the vapour of methyl alcohol is passed over finely-divided copper (obtained by reducing cupric oxide) heated at 300°C., it under-goes decomposition into formaldehyde and hydrogen :

$$\underset{\text{Mehyl alcohol}}{CH_3OH} \rightarrow \underset{\text{Formaldehyde}}{H.CHO} + H_2$$

(3) *From Formic Acid.* Formaldehyde, H.CHO, on oxidation yields formic acid, H.COOH. Conversely, it may be obtained from formic acid by *reduction.* There are three different methods by which this may be done :

(*i*) *By Distilling the Calcium Salt of Formic Acid :*

$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \rightarrow \underset{\text{Formaldehyde}}{H.CHO} + \underset{\text{Calcium carbonate}}{CaCO_3}$$

Here a part of the formate radical is oxidized to the carbonate radical at the expense of the other part which is reduced to formaldehyde.

(*ii*) *By Catalytic Auto-reduction of Formic Acid.* In this method the vapour of formic acid is passed over titanium oxide heated at 300°C. :—

$$\underset{\text{(two molecules)}}{\begin{matrix} H.CO.OH \\ : \\ H.COO.H \end{matrix}} \rightarrow \underset{\text{Formaldehyde}}{H.C\leqslant^{H}_{O}} + H_2O + CO_2$$

Formic acid

The reaction is an instance of *auto-oxidation and reduction* : one molecule is oxidized to carbonic acid at the expense of another, which is reduced to formaldehyde.

(*iii*) *By Catalytic Reduction of Formyl Chloride* (**Rosenmund's method**). In this method, the chloride of formic acid is reduced by means of hydrogen in the presence of platinized barium sulphate (*i.e.*, finely-divided platinum precipitated on $BaSO_4$.) :—

$$\underset{\text{Formyl chloride}}{H.COCl} + H_2 \rightarrow \underset{\text{Formaldehyde}}{H.C\leqslant^{H}_{O}} + HCl.$$

(4) *By Hydrolysis of Methylene Chloride.* When methylene chloride is hydrolysed by means of superheated water, the dihydric alcohol is first formed, which loses the elements of water, yielding formaldehyde :—

$$\underset{\substack{\text{Methylene}\\\text{chloride}}}{H.CH_2Cl_2} + 2H.OH \longrightarrow \underset{\substack{\text{Methylene glycol}\\\text{(unstable)}}}{H.CH(OH)_2} + 2HCl$$

$$H.CH(OH)_2 \longrightarrow \underset{\text{Formaldehyde}}{H.C\leqslant^{H}_{O}} + H_2O$$

Physical Properties. Formaldehyde is a gas, having a very pungent odour. It is soluble in water, alcohol, and ether.

8. Reactions of Formaldehyde The reactions of formaldehyde may be studied under three main heads :—

(*A*) **Reactions in which Formaldehyde resembles Ketones and other Aldehydes** (*Reactions of the Carbonyl Group*). Formaldehyde gives all the general reactions of aldehydes and ketones described in Sec. 4

(*B*) **Reaction in which Formaldehyde resembles other Aldehydes but not Ketones :—**

(1) *Reducing Power.* Formaldehyde is an active reducing agent, being readily converted into formic acid :—

$$H.C\overset{H}{\underset{O}{\leqslant}} \quad + \quad O \rightarrow \quad H.C\overset{OH}{\underset{O}{\leqslant}}$$

Formaldehyde — Formic acid

(2) *Polymerization.* Formaldehyde resembles other aldehydes in being readily polymerized. When an aqueous solution of formaldehyde is evaporated, we get **paraformaldehyde**, $(H_2CO)_n$, which is a white crystalline solid melting at 63° and of unknown molecular weight. This substance when heated is reconverted into formaldehyde, which shows that it is a true polymeride of formaldehyde Several other polymerides of formaldehyde are known.

(3) *Schiff's Reaction.* See *p.* 118.

(*C*) **Reactions in which Formaldehyde differs from other Aliphatic Aldehydes :—**

(1) **Cannizzaro's Reaction**. When treated with a solution of caustic alkali, formaldehyde undergoes auto-oxidation, one molecule being oxidized to formic acid at the expense of another which is reduced to methyl alcohol :

$$2H.CHO + KOH \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Potassium formate}}{H.COOK}$$

Formaldehyde

Aromatic aldehydes (*e.g.*, benzaldehyde, $C_6H_5.CHO$) also give Cannizzaro's reaction.

(2) *Reaction with ammonia.* Unlike other aldehydes, formaldehyde when treated with ammonia, does not yield aldehyde ammonia but **hexamethylene tetramine**, $(CH_2)_6N_4$. This is a crystalline substance and is used in medicine, under the name of **hexamine or urotropine** as an internal disinfectant.

(3) *Reaction with Proteins.* An aqueous solution of formaldehyde possesses the power of transforming proteins into a hard, elastic rubber-like mass.

(4) *Rimini's Test.* See under Expt 7

9. Tests of Formaldehyde. Formaldehyde gives the following tests, of which the last one is characteristic :—

Expt 7 *Tests of Formaldehyde* —

(1) *Silver Mirror Test.* (See Expt 1)

(2) *Reduction of Fehling's solution.* (See Expt 3

(3) *Schiff's Test* (See Expt. 4)

(4) **Rimini's Test** Add to an aqueous solution of formaldehyde two drops of Phenylhydrazine, and then a drop of dilute freshly prepared solution of sodium nitroprusside and a few drops of sodium hydroxide. Notice the formation of a deep blue colour, which changes through green and brown to red

Uses. Formaldehyde is usually employed as a 40 per cent.

aqueous solution, called **formalin**. The following are its important uses :

(*1*) As a *disinfectant*. Formalin diluted with water is employed for sterilizing surgical instruments, whilst paraformaldehyde or "*paraform*," because of its ready conversion into gaseous formaldehyde, is employed for disinfecting rooms.

STANISLAO CANNIZZARO
(1826-1910)

was an Italian chemist who discovered the reaction known after his name

(2) On account of its power of *rendering protein insoluble in* water, formaldehyde is employed for the preservation of anatomical. It is specimens and for fixing the gelatin film on photographic plates.

(3) Formaldehyde is also employed in the manufacture of.

(*i*) **Urotropine** (*p.* 120) :

(*ii*) **Bakelite,** a thermosetting plastic used as an insulator. It is prepared by the action of formaldehyde on phenol;

(*iii*) **Galalith** or artificial horn, got by the action of formaldehyde on casein of milk;

(*iv*) **Rongalite,** a substance obtained by boiling a solution of the bisulphite compound of formaldehyde with zinc-dust.

$$H.CH<\begin{matrix}OH\\SO_2Na\end{matrix} + 2H \rightarrow H\,CH<\underset{\text{Rongalite}}{\begin{matrix}OH\\SO_2Na\end{matrix}} + H_2O.$$

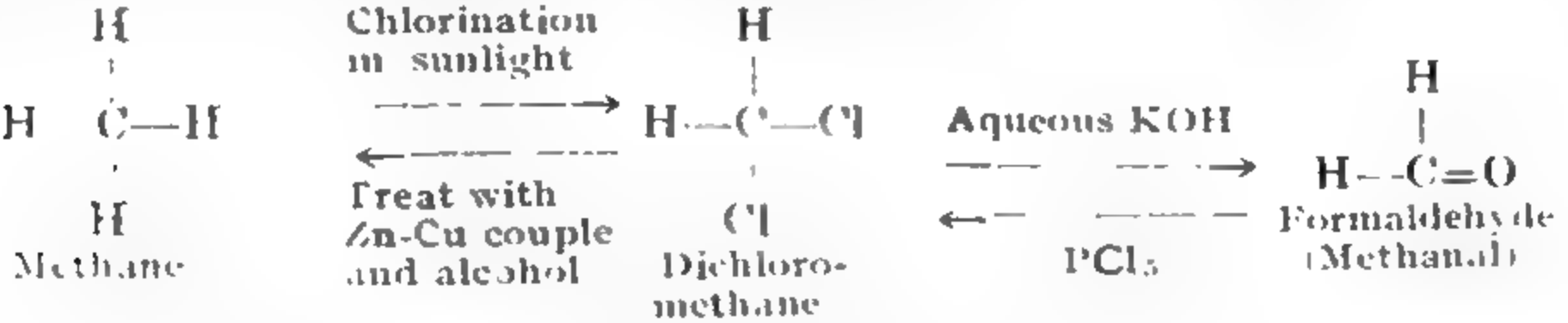
and used as a reducing agent in vat-dying.

10. Constitution. The molecular formula of formaldehyde, as determined by combustion and molecular weight determination is $\mathbf{CH_2O}$.

Since carbon, oxygen, and hydrogen are tetra-, di-, and monovalent, respectively, there is only one structure possible for formaldehyde, *viz.*,

This structure is fully supported by the reactions of formaldehyde and its formation from methylene chloride.

From the above formula it is evident that formaldehyde is a **derivative of methane** in which two of the hydrogn atoms have been replaced by oxygen (hence the name **methanal**). This structural relationship is proved by the following interconversions:



11. Acetaldehyde, *Ethanal*, $CH_3.C\leqslant^{H}_{O}$

Formation. Acetaldehyde may be obtained by methods similar to those described in the case of formaldehyde (Sec. 7)

They may be summarized as under:—

(1) By the oxidation of Ethyl Alcohol:

$$\underset{\text{Ethyl alcohol}}{CH_3\ CH_2OH} + O \rightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2O$$

It is by this reaction that acetaldehyde is usually prepared in the laboratory.

(2) By passing the vapour of ethyl alcohol over heated, finely divided copper (catalyst) :

$$CH_3.CH_2OH \rightarrow CH_3.CHO + H_2$$

(3) *From Acetic Acid.* This may be done in three different ways :

(*i*) By distilling a mixture of calcium acetate and calcium formate:

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2\ Ca} + \underset{\text{Calcium formate}}{(HCOO)_2\ Ca} \rightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$$

(*ii*) By passing a mixture of acetic acid and formic acid, in the vaporous state, over titanium oxide at 300°:

$$\begin{matrix} CH_3COOH \\ \\ HCOOH \end{matrix} \longrightarrow CH_3C\leqslant^{H}_{O} + CO_2 + H_2O$$

Acetaldehyde

(*iii*) By reducing acetyl chloride by means of hydrogen in the presence of platinized barium sulphate (Rosenmund's method):

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \rightarrow \underset{\text{Acetaldehyde}}{CH_3C\leqslant^{H}_{O}} + HCl$$

(4) By hydrolysing ethylidene chloride with superheated water :

$$CH_3.CHCl_2 \xrightarrow{H.OH} CH_3.CH(OH)_2 \xrightarrow{-H_2O} CH_3.CHO$$

Ethylidene chloride — Ethylidene glycol (unstable) — Acetaldehyde

Laboratory Preparation. Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol by means of potassium dichromate and dilute sulphuric acide:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$CH_3.CH_2OH + O \rightarrow CH_3.CHO + H_2O \qquad [\times 3]$$

$$3CH_3.CH_2OH + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3CH_3.CHO + K_2SO_4 + Cr(SO_4)_3 + 7H_2O$$

To avoid further oxidation of acetaldehyde, an excess of alcohol must be employed.

Expt. 8. A ½ litre distillation flask is fitted with a dropping funnel, and is connected to a condenser and a receiver, the latter being cooled by a freezing mixture (Fig. 2).

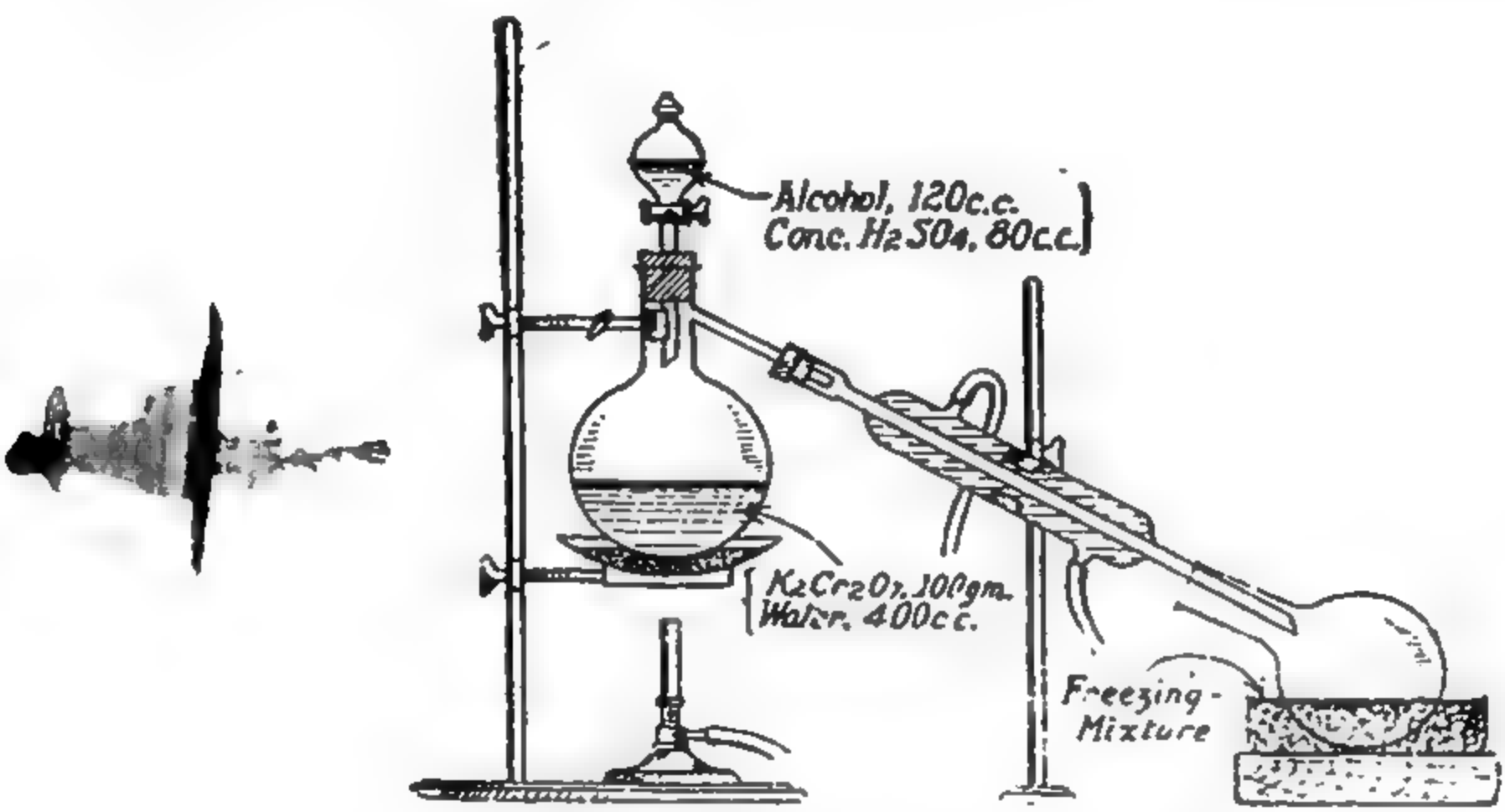


Fig. 2. Preparation of Acetaldehyde.

100 grams of coarsely powdered potassium dichromate and 400 ml. of water are placed in the flask, which is gently heated on a sand bath, until the liquid just boils. A mixture of 120 ml. alcohol and 80 ml. concentrated sulphuric acid is then slowly run in from the tap funnel. During this addition, the reaction should proceed at such a rate as to keep the liquid boiling. When all has been added, the boiling is continued, until 150 ml. of the distillate have been collected. The distillate contains water and alcohol in addition to aldehyde.

The aldehyde cannot be completely separated from this mixture by fractional distillation. It is, therefore, purified by conversion into aldehyde ammonia. The process consists of the following three steps:—

(i) *Preparation of Ethereal Solution.* The flask containing the crude aldehyde is fitted with a reflux condenser (Fig. 3.). The upper end of the condenser is connected by means of a long tube to two "reversed" wash-bottles, each containing about 50 ml. of ether, and cooled by a freezing mixture. The condenser is supplied with water at 30—35°C. A few glass beads are placed in the flask and the liquid gently boiled for 15 minutes. During this time, most of the aldehyde (b. p. 21°C) would have passed over into the ether. Alcohol and water condense and flow back into the flask.

(ii) *Saturation with Ammonia.* The etheral solution of aldehyde, prepared as above, is now saturated with *dry* ammonia gas (prepared by dropping concentrated ammonia solution on to caustic soda stricks contained in a filtration flask, and passing

the gas through a tower containing caustic soda sticks or pieces of quicklime. The passage of the gas is continued, until the solution smells strongly of ammonia. The solution is left in the freezing mixture for an hour or so, when the crystals of aldehyde ammonia separate out. These are filtered at the pump, washed with a little dry ether, and finally dried in a desiccator.

(iii) *Decomposition of Aldehyde Ammonia.* The aldehyde ammonia is now distilled with dilute sulphuric acid from a water bath, and the evolved aldehyde is collected in a well-cooled receiver. The distillate is dried over anhydrous calcium chloride and redistilled.

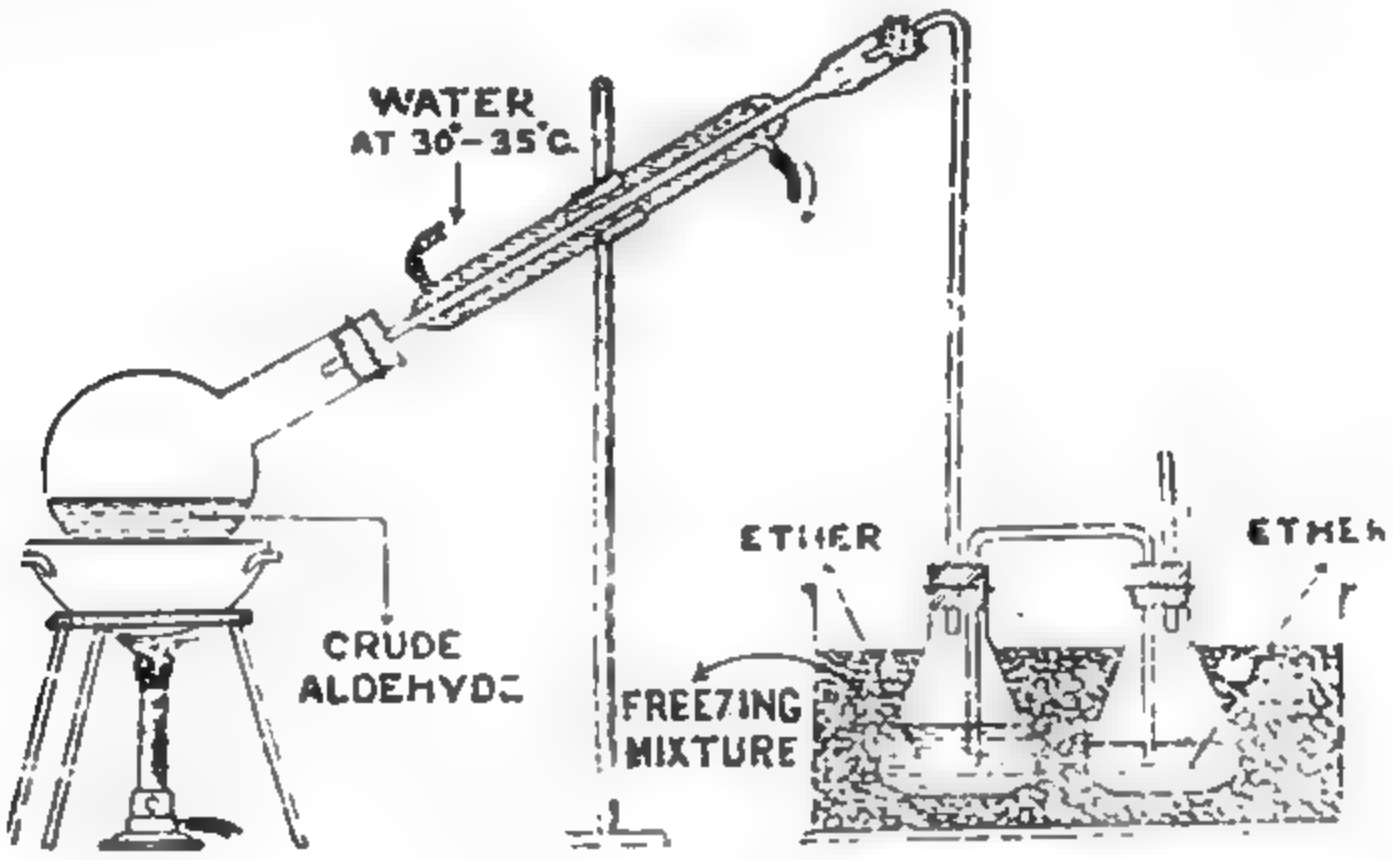


Fig. 3. Preparation of Aldehyde Ammonia.

Manufacture. Acetaldehyde is now manufactured from acetylene (see chap. 8, Sec. 5).

Physical Properties. Acetaldehyde is a colourless mobile liquid, possessing a characteristic, suffocating odour and boiling at 21° C. It is readily soluble in water, alcohol and ether.

Reactions. Acetaldehyde gives all the reactions described in Secs. 4 and 5. They may be summarized as under:—

(A) **Reactions common to all Aldehydes and Ketones,** *i.e.*, Reactions of the $>CO$ Group:—

Addition Reactions. Acetaldehyde combines with (*i*) hydrogen, (*ii*) hydrogen cyanide, and (*iii*) sodium bisulphite:

(*i*) $CH_3C\leqslant^{H}_{O} + 2H \rightarrow CH_3.CH_2OH$
Ethyl alcohol

(*ii*) $CH_3C\leqslant^{H}_{O} + HCN \rightarrow CH_3.C(OH)(H)(CN)$
Acetaldehyde cyanhydrin

(*iii*) $CH_3C\leqslant^{H}_{O} + NaHSO_3 \rightarrow CH_3C(OH)(H)(SO_3Na)$
Acetaldehyde sodium-bisulphite

(2) *Substitution of Carboxylic Oxygen.* Acetaldehyde reacts with

(*i*) hydroxylamine, (*ii*) phenylhydrazine, and (*iii*) phosphorus pentachloride :—

(*i*) $CH_3C\leqslant^{H}_{O} + H_2NOH \rightarrow CH_3.C\leqslant^{H}_{NOH} + H_2O$

Acetaldoxime

(*ii*) $CH_3C\leqslant^{H}_{O} + H_2N.NH.C_6H_5 \rightarrow CH_3.C\leqslant^{H}_{N.NH\,C_6H_5} + H_2O$

Acetaldehyde Phenylhydrazone

(*iii*) $CH_3.C\leqslant^{H}_{O} + PCl_5 \rightarrow CH_3C(H)(Cl)(Cl) + POCl_3$

Ethylidene chloride

(*B*) **Reactions that differentiate Aldehydes from Ketones :**

(1) *Reducing Power.* See Sec. 5.

(2) *Polymerization.* Acetaldehyde, in the presence of suitable catalysis, polymerizes to give the following products :—

(*i*) **Aldol.** When a dilute alkali solution is added to acetaldehyde we get *aldol*[1]—a substance having the same empirical formula as acetaldehyde but with double the molecular weight. This is a colourless liquid, possessing characteristic properties of an aldehyde and also the properties of an alcohol. For this reason, it must be assumed that while the aldehyde group of one of the molecules undergoing combination remains intact, the oxygen atom of the CHO group of the other forms a hydroxyl group. Further, the change is non-reversible : hence the combination between the molecules must be assumed to have taken place through a carbon-carbon chain. The reaction is referred to as **aldol condensation.**[2]

$$CH_3.C\leqslant^{H}_{O} + H\,CH_2\,CHO \rightarrow CH_3.CH(OH).CH_2.CHO$$

Aldol (β-Hydroxy-butyraldehyde)

(*ii*) **Ethyl Acetate.** Under the catalytic influence of aluminium ethoxide, acetaldehyde yields ethyl acetate. The reaction is employed on a commercial scale. Here two molecules of the aldehyde unite in such a manner that the aldehydic hydrogen atom of one goes to the carbonylic carbon of the other :

$$CH_3.CHO + OHC.CH_3 \rightarrow CH_3\,CO.OCH_2.CH_3$$

Ethyl acetate

(*iii*) **Paracetaldehyde.** If a few drops of concentrated sulphuric acid be added to acetaldehyde (b p 21°C), the mixture becomes warm, and, then begins to boil violently. When the reaction is over, the liquid is found to boil at 124°, and has a molecular weight three times that of the original acetaldehyde. The new liquid, known as paracetaldehyde, is converted back into acetaldehyde on being distilled with dilute sulphuric acid. The conversion of acetaldehyde into paracetaldehyde is, therefore, a reversible reaction and the union between the molecules must be assumed to have taken place through oxygen linkages:—

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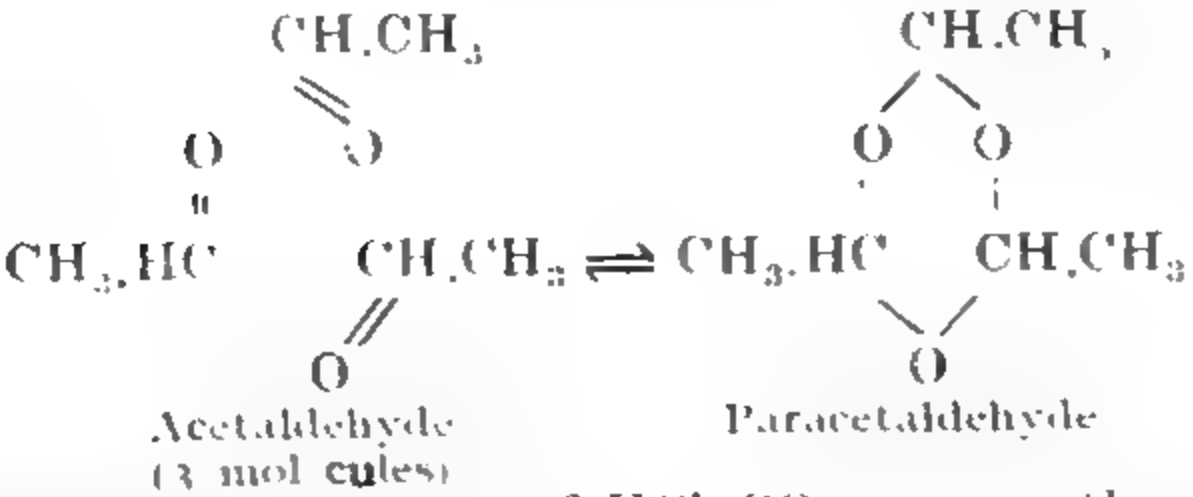
[1] The term *aldol* refers to aldehyde-alcohol, the compound possessing the properties of both an aldehyde and an alcohol.

[2] The term *condensation* is explained in Sec. 14.



(*ii*) **Metaldehyde**. If a trace of HCl, SO_3, or another acid is added to acetaldehyde cooled below 0°, four molecules of the aldehyde undergo combination, yielding metaldehyde:—

$$4CH_3CHO \rightarrow (CH_3CHO)_4$$

Metaldehyde

The structure of metaldehyde has not been determined as yet.

(3) *Schiff's Reaction*. Acetaldehyde gives this reaction (*see* Expt. 4, *p.* 117).

(4) *Resinification with Alkalies*. See *p.* 117.

(5) *Formation of Aldehyde ammonia* See *p.* 118.

(6) *Formation of Acetal* See *p.* 146.

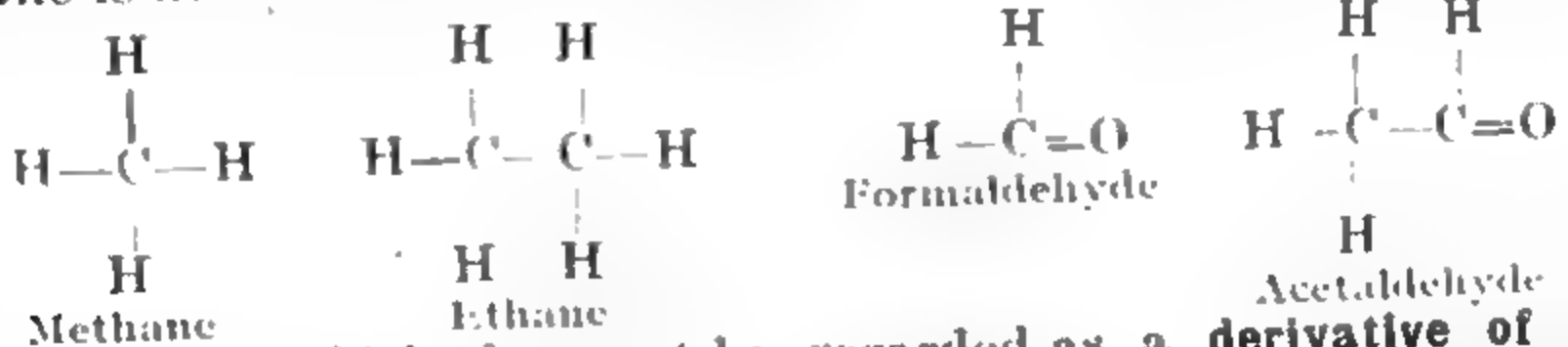
Tests. Besides the tests given in Sec. 6, which are common to all aldehydes, acetaldehyde gives the following specific tests :

(*i*) It gives a cherry-red colour with a solution of sodium nitroprusside and caustic soda.

(*ii*) It gives a blue colour with sodium nitroprusside and piperidine.

Uses. Acetaldehyde is employed in the manufacture of acetic acid, ethyl acetate, certain dyes and drugs.

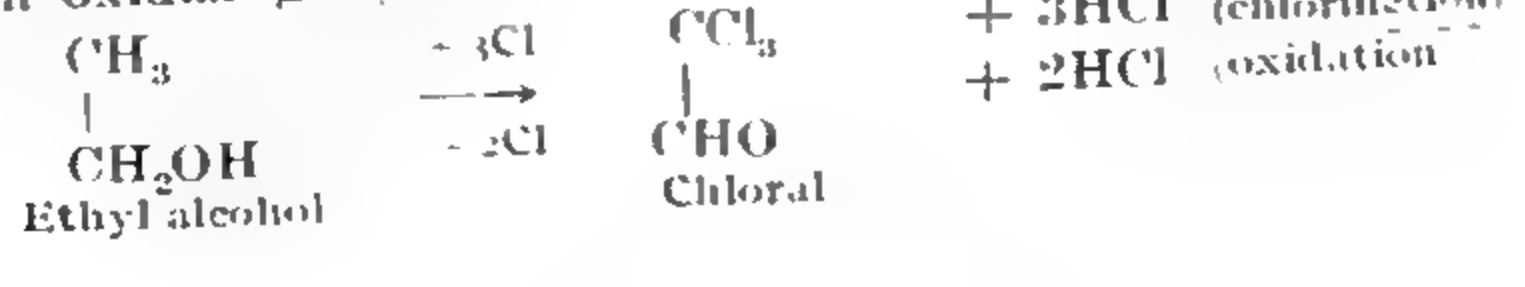
12. Constitution of Acetaldehyde Acetaldehyde closely resembles formaldehyde in chemical behaviour, and its molecular formula is C_2H_4O as against CH_2O of formaldehyde It must, therefore, be regarded as the next **homologue of formaldehyde**, being derived from the latter by the replacement of a hydrogen atom, by a methyl group, just as ethane is derived from methane.



Further, acetaldehyde must be regarded as a **derivative of ethane**, being derived from the latter by the replacement of two hydrogen atoms linked to one and the same carbon atom by an oxygen atom ; hence the name **ethanal**.

13. Chloral. *Trichloroacetaldehyde*, $CCl_3.CHO$.

Preparation. This substance is obtained from alcohol by the prolonged action of dry chlorine, first at the ordinary temperature, and then at the boiling point. Chlorine here acts both as a chlorinating and an oxidizing agent : —



The crystalline reaction product, which consists mainly of *chloral alcoholate* $CCl_3.CH<^{OH}_{OC_2H_5}$, is distilled with concentrated sulphuric acid. The oily distillate of crude chloral is converted into chloral hydrate, $CCl_3\,CH(OH)_2$, which is purified by recrystallization and then distilled with sulphuric acid, when pure chloral passes over.

Physical Properties. Chloral is an oily liquid of penetrating odour (b.p. 97°).

Reactions. Chloral possesses the general reactions of an aldehyde: it gives the silver mirror test, combines directly with ammonia, hydrogen cyanide, sodium bisulphite, etc., and reacts with hydroxylamine and phenylhydrazine. On oxidation with concentrated nitric acid, it yields trichloroacetic acid (compare acetaldehyde, which gives acetic acid):

$$CCl_3.CHO + O \rightarrow CCl_3.COOH.$$

When boiled with a solution of potassium hydroxide, chloral decomposes to give chloroform and potassium formate,

$$CCl_3.CHO + KOH \rightarrow CHCl_3 + HCOOK,$$

the reaction being often employed for preparing pure chloroform.

Chloral combines with water to form **chloral hydrate**:-

Chloral — Chloral hydrate

14. Chloral Hydrate, $CCl_3.CHO + H_2O$, or $CCl_3.CH(OH)_2$. As already mentioned, chloral combines with one molecular proportion of water, yielding chloral hydrate. This substance forms colourless crystals, readily soluble in water and melting at 57°.

Constitution. The evidence as to the constitution of chloral hydrate is not conclusive. In certain respects, it resembles aldehydes, while in others it offers a striking contrast to their behaviour. Thus, like aldehydes, it gives the silver-mirror test, and reacts with hydroxylamine yielding an oxime. Hence it should be given the aldehyde structure $CCl_3.CHO+H_2O$. However, unlike the aldehydes, it does *not* polymerize and does *not* give the Schiff's test. Hence, it is usually ascribed the structure $CCl_3.CH(OH)_2$. This fact is of theoretical interest, for chloral hydrate is one of the very few compounds containing two hydroxyls linked to a single carbon atom.

Use. Chloral hydrate is used in medicine as a drug for producing sleep.

15. Acetone. *Dimethyl-ketone, Propanone,* $CH_3.CO.CH_3$

Occurrence. Acetone occurs in minute quantities in blood and normal urine; in cases of diabetes and acetonuria, the proportion is much greater.

Formation. Acetone may be obtained by the following methods, which should be compared with those employed in the case of formaldehyde and acetaldehyde:

(1) By the oxidation of isopropyl alcohol (which is a *secondary* alcohol):—

$$\underset{\text{Isopropyl alcohol}}{\overset{CH_3}{\underset{CH_3}{>}}CH.OH} + O \rightarrow \underset{\text{Acetone}}{\overset{CH_3}{\underset{CH_3}{>}}CO} + H_2O$$

(2) By passing the vapour of isopropyl alcohol over heated, finely-divided copper (catalyst) :—

$$(CH_3)_2CH.OH \longrightarrow (CH_3)_2CO + H_2$$

(3) *From Acetic Acid.* This may be done in two ways :

(*i*) By the dry-distillation of calcium acetate :—

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \longrightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3} + CaCO_3$$

This method is employed for the preparation of acetone in the laboratory (*see* Expt. 9) and on the large scale.

(*ii*) By passing the vapour of acetic acid over precipitated aluminium oxide at 400° C :—

$$\begin{matrix} CH_3COOH \\ CH_3COOH \\ \text{(Acetic acid (2 molecules)} \end{matrix} \longrightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3} + H_2O + CO_2$$

(4) By hydrolysing 2 : 2-dichloropropane with superheated water :—

$$\underset{\text{2 : 2-dichloropropane}}{CH_3.CCl_2.CH_3} \xrightarrow{HOH} \underset{\substack{\text{Unstable dihydroxy} \\ \text{compound}}}{CH_3.C(OH)_2.CH_3} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

Laboratory Preparation. In the laboratory, acetone is most conveniently prepared by the dry-distillation of calcium acetate :—

$$(CH_3COO)_2Ca \longrightarrow CH_3.CO.CH_3 + CaCO_3$$

Expt 9 Place 100 grams of dried calcium acetate in a retort (or large size test tube) attached to a Liebig condenser (Fig 4). Heat the retort by means of a luminous flame kept in constant motion. Dilute the distillate, which contains some tarry matter, with an equal volume of water, and filter through a fluted filter paper. The filtrate, which consists of an aqueous solution of acetone may be directly employed for showing the tests of acetone as in Expt. 10.

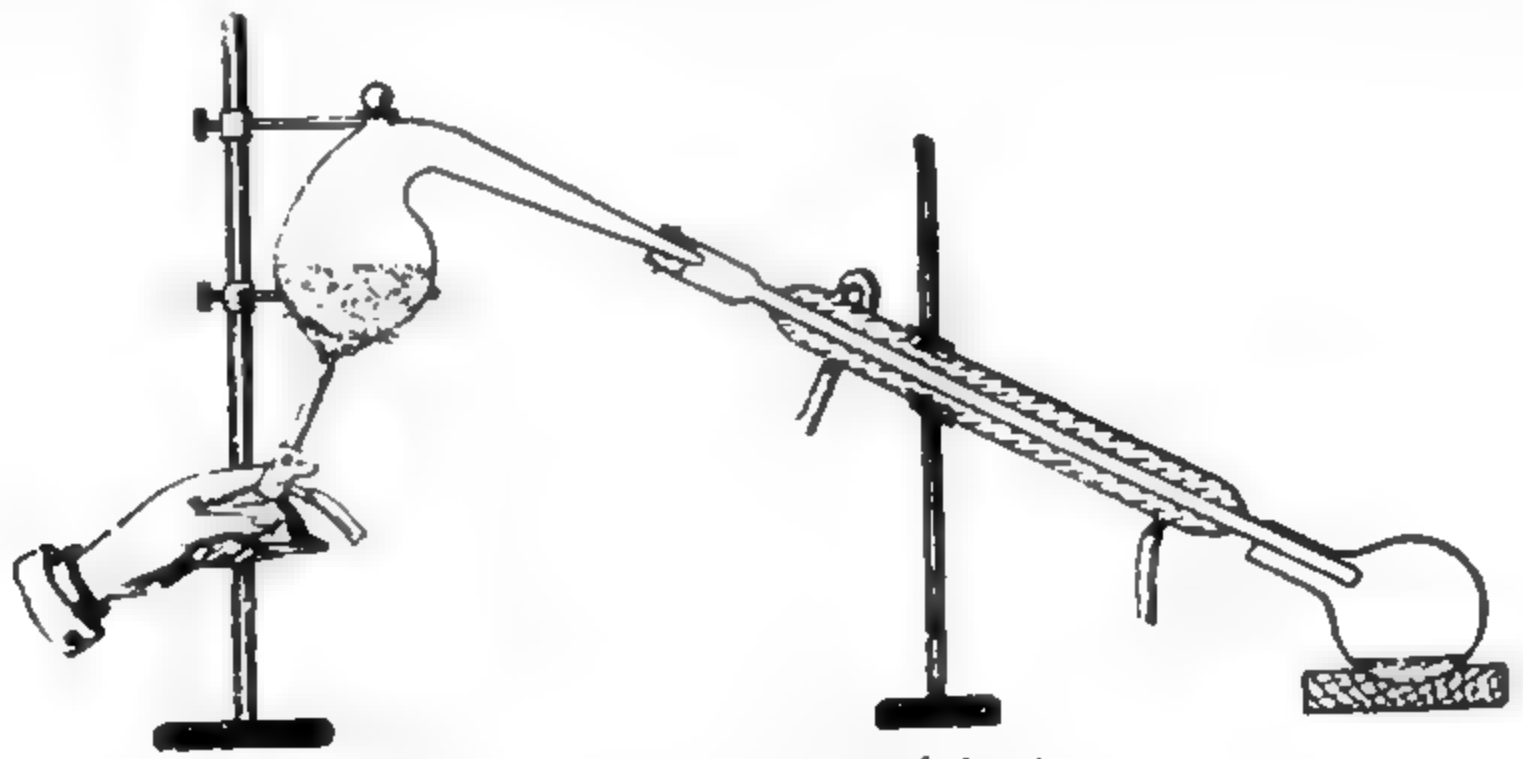


Fig. 4. Preparation of Acetone.

If it is desired to prepare a pure sample of acetone from the aqueous solution obtained as above, the latter should be fractionated, and the portion passing over between 50° and 60° collected separately. This is then mixed with a strong solution of sodium bisulphite. The crystals of *acetone sodium bisulphide*, which separate after a short time, are pressed between folds of filter paper, and then decomposed by distilling with a solution of sodium carbonate, when acetone passes over :—

$$2(CH_3)_2C\!<\!\begin{matrix}OH\\SO_3Na\end{matrix} + Na_2CO_3 \rightarrow 2(CH_3)_2CO + 2Na_2SO_3 + H_2O + CO_2$$

The distillate is allowed to stand over fused calcium chloride, to remove water, and then distilled.

Manufacture. Acetone is of great commercial importance and is manufactured from the different sources :—

(1) ***From Wood Distillation.*** Wood distillation has long been the source of acetone in two ways, acetone being obtained (*a*) directly, and (*b*) from the acetic acid, by dry distillation of the calcium salt of the latter.

(*i*) Crude acetone and crude wood spirit, obtained by the fractional distillation of *pyroligneous acid* (Sec. 92), contain both acetone and methyl alcohol. Each of these fractions is separately shaken with a saturated solution of sodium bisulphite, and the crystals of bisulphite and the crystals of bisulphite compound, after being separated by centrifuging, are decomposed by warming with sodium carbonate solution The acetone set free is distilled off, dried with calcium chloride, and then redistilled.

(*ii*) Alternately, acetone is prepared by the dry disitllation of calcium acetate (obtained from pyroligneous acid). The distillate is fractionated, and the fraction passing at 50 to 60 is collected separately. This is mixed with a strong solution of sodium bisulphite, when crystals of the acetone sodium bisulphite are formed. These are separated and decomposed as described above.

(2) ***From Starch.*** Acetone is also manufactured by the fermentation of starch by means of **Bacillus maceranus,** *n*-butyl alcohol being obtained as a by-product.

(3) ***From Acetic Acid.*** Acetone is nowadays manufactured by passing the vapour of acetic acid over alumina or thoria at 300—380 C.

$$2CH_3COOH \longrightarrow CH_3.CO.CH_3 + H_2O + CO_2$$

Physical Properties. Acetone is a colourless liquid, having a pleasant, peppermint-like odour. It boils at 56°C. It is perfectly miscible with water, alcohol and ether.

Reactions. Acetone gives all the reactions of the carbonyl group, (Sec. 4). They may be summarised as follows :—

(1) *Addition Reactions.* Acetone combines with (*i*) hydrogen, (*ii*) hydrogen cyanide, and (*iii*) sodium bisulphite :

(*i*) $$CH_3.CO.CH_3 + 2H \longrightarrow \underset{\text{Isopropyl alcohol (a secondary alcohol)}}{CH_3.CH(OH).CH_3}$$

(*ii*) $$(CH_3)_2C{=}O + H.CN \longrightarrow \underset{\text{Acetone cyanhydrin}}{(CH_3)_2C{<}^{OH}_{CN}}$$

(*iii*) $$(CH_3)_2C{=}O + NaHSO_3 \longrightarrow \underset{\text{Acetone sodium bisulphite}}{(CH_3)_2C{<}^{OH}_{SO_3Na}}$$

This last reaction is utilised for the separation of acetone from a mixture.

(2) *Substitution of Carbonylic Oxygen.* Acetone reacts with (*i*) hydroxylamine, (*ii*) phenylhydrazine, and (*iii*) phosphorus pentachloride :

(*i*) $$(CH_3)_2CO + H_2NOH \longrightarrow \underset{\text{Acetoxime}}{(CH_3)_2C{=}NOH} + H_2O$$

(*ii*) $(CH_3)_2CO + H_2N.NH\,C_6H_5 \longrightarrow (CH_3)_2C{=}N.NH\,C_6H_5 + H_2O$
Acetone phenylhydrazone

(*iii*) $CH_3.CO.CH_3 + PCl_5 \longrightarrow CH_3.CCl_2.CH_3 + POCl_3$
2 : 2-Dichloropropane

Reactions in which Acetone differs from Aldehydes. Acetone does not give the reactions discussed in Sec. 13. The following reactions further differentiate acetone (and other ketones) from aldehydes:-

(1) *Oxidation.* As already stated, acetone does not possess reducing properties and consequently does not react with mild oxidizing agents, such as ammoniacal silver nitrate or Fehling solution. When submitted to vigorous oxidation, it breaks up, yielding acetic acid, carbon dioxide and water :

$$CH_3.CO.CH_3 + 4O \rightarrow CH_3COOH + H_2O + CO_2$$

(2) *Condensation with Elimination of Water.* When treated with a dehydrating agent acetone yields the following three products, the first two being obtained by saturating acetone with dry hydrogen chloride and keeping the solution for some time, and the third by distilling it with concentrated sulphuric acid:-

(*i*) **Mesityl Oxide :**

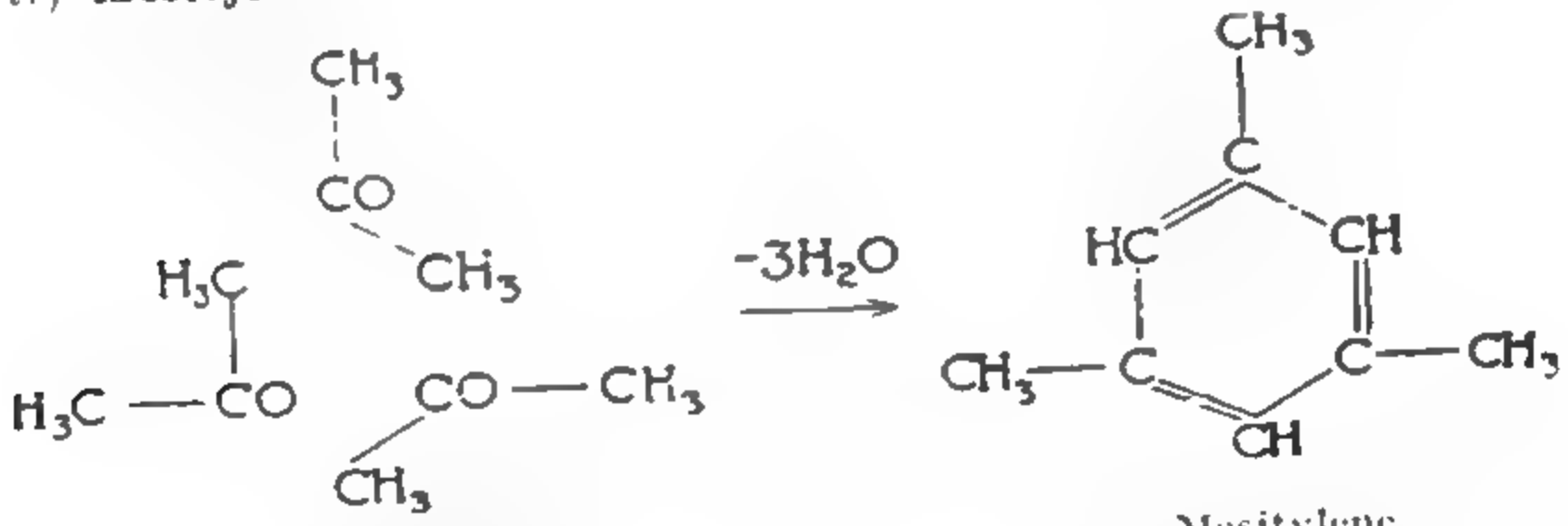
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2CH.CO.CH_3 \xrightarrow{-H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH.CO.CH_3$$
Acetone (2 molecules) — Mesityl oxide

(*ii*) **Phorone :**

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2CH.CO.CH + H_2 + O\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{2H_2O}$$
Acetone (3 molecules)

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH.CO.CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$$
Phorone

(*iii*) **Mesitylene :**



Acetone (3 molecules) — Mesitylene

In the above reactions, two hydrogen atoms attached to a carbon atom that is in *direct* union with the -CO group are removed along with the carbonylic oxygen of another molecule.

Similarly, two or more molecules of other ketones may undergo condensation *with elimination of water*. On the other hand, aldehydes are capable of undergoing aldol condensation (Sec. 13), in which no water is eliminated.

Tests. Acetone may be identified by the tests described in the following experiment:

Expt. 10. *Tests of Acetone.* Use the aqueous distillate from Expt. 9 for the following tests :—

(1) *Legal's Test.* Take about 5 ml. of dilute acetone solution in a test tube, add about 1 ml. of sodium hydroxide, and then about 5 drops of a freshly prepared solution of sodium nitroprusside (5 per cent). A ruby-red colour is produced which fades to yellow on standing.

Repeat the above test, and acidify the solution at once with acetic acid. A purple-red colour is produced.

(2) *Idofoim Reaction.* (*a*) Acetone gives iodoform reaction in the cold. Take about 2 ml. of dilute acetone solution, add about 5 drops of sodium hydroxide and then add a decinormal iodine solution, drop by drop, until the liquid becomes faintly yellow. There occurs an immediate separation of iodoform.

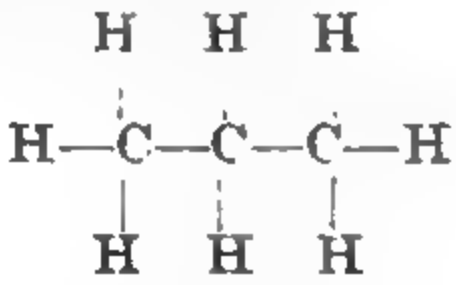
(*b*) Repeat the above test, using ammonia instead of sodium hydroxide. On adding iodine, drop by drop, a small amount of a black precipitate of nitrogen iodide is formed. Allow to stand, or warm. The precipitate disappears and iodoform is produced *This reaction serves to distinguish acetone from ethyl alcohol.*

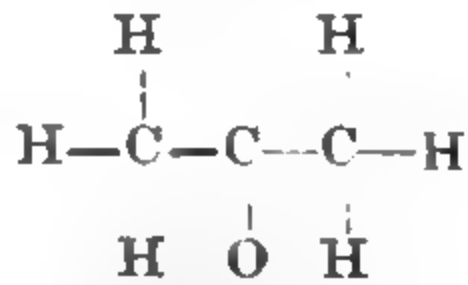
Formation of Indigo. Dissolve a small quantity of *o*-nitrobenzaldehyde in about 1 ml. of acetone, stir the solution into about 100 ml. of water containing a little sodium hydroxide. Notice the rapid formation of indigo-oblue

Uses. (1) Acetone is an important solvent, and is used in the preparation of high-class varnishes, cordite, and collodion, and for storing acetylene. It is also employed for extracting resins from wood and for making paint and varnish removers.

(2) It is used in the preparation chloroform, iodoform, and synthetic rubber.

Constitution. The structure of acetone follows from its preparation from calcium acetate and 2 : 2-dichloropropane and is fully supported by its chemical behaviour. As will be seen from the following structural formulae, acetone is a derivative of propane, hence the name **propanone** :—


Propane


Propanone
(Acetone)

16. Polymerization and Condensation :—

(1) **Polymerization.** The term "polymerization," in its *general* sense, is applied to any reaction involing the *direct union of two or more molecules of a substance to form a new compound, whose molecular weight is a multiple of that of the orginal substance.* Thus, acetylene, when passed through a red-hot tube, polymerizes to benzene :—

$$\underset{\text{Acetylene}}{3C_2H_2} \rightarrow \underset{\text{Benzene}}{C_6H_6}$$

In the restricted sense that the term "polymerization" is applied in organic chemistry it refers to the union of two or more molecules of a substance to from a new compound *capable of reconversion into the original substance.* Conversion of acetaldehyde into paracetaldehyde (Sec. 13) and of formaldehyde into paraformaldehyde (Sec. 12) are typical examples of polymerization.

(2) **Condensation.** This term is applied to the *union of molecules, or part of the same molecule, through carbon bonds (or carbon-nitrogen bonds), with the production of a substance from which the original compound* (or

compounds) cannot be regenerated by a simple reaction.

Condensation may occur : (*i*) between molecules of the same substance or different substances (external condensation) or (*ii*) between parts of the same molecule (internal condensation). It may or may not be accompanied by loss of water alcohol, ammonia, etc. Examples of *externa'* condensation are ;

(*i*) Conversion of acetylene into benzene (Chap. 8, Sec. 5).

(*ii*) Condensation of aldehydes and ketones with hydroxylamine and phenylhydrazine (*p.* 130).

(*iii*) Aldol condensation. (Sec. 13)

(*iv*) Conversion of acetone to mesityl oxide, phorone and mesitylene (*p.* 130)

An example of *internal* condensation is the conversion of the ammonium salt of succinic acid into succinimide by the action of heat :

$$\begin{matrix} CH_2.COONH_4 \\ | \\ CH_2.COONH_4 \\ \text{Ammonium succinate} \end{matrix} \rightarrow \begin{matrix} CH_2.CO \\ \diagdown \\ \quad NH \\ \diagup \\ CH_2.CO \\ \text{Succinimide} \end{matrix} + 2H_2O + NH_3$$

17 Crotonic Aldehyde *Crotonaldehyde.* $\triangle$-*2-Butenal.* $CH_3CH=CH.CHO$ This is an example of an *unsaturated* aldehyde, and is derived from a homologue of ethylene, *viz.*, symmetrical dimethyl-ethylene or $\triangle$-2-butene[1], $CH_3CHC=HCH_3$.

Crotonic aldehyde may be obtained from acetaldehyde through aldol. The latter substance, when submitted to distillation, or treated with a dehydrating agent, loses a molecule of water, yielding crotonic aldehyde

$$\begin{matrix} CH_3.CH(OH).CH_2.CHO \\ \text{Aldol or } \beta \text{ hydroxybutyraldehyde} \end{matrix} \rightarrow \begin{matrix} CH_3.CH=CH.CHO \\ \text{Crotonic aldehyde} \end{matrix} - H_2O$$

Crotonic aldehyde is a colourless, pungent-smelling liquid (b.p. 105°). It shows the typical properties of aldehydes described in Sec. 9 and 10. It gives the silver mirror test and Schiff's test. On oxidation with silver oxide, it gives crotonic acid, $CH_3.CH=CH.COOH$.

In addition to the aldehydic characters, crotonic aldehyde shows the behaviour of an unsaturated compound. Thus, with bromine it gives the dibromide, $CH_3.CHBr.CHBr.CHO$. Catalytic hydrogenation, in the presence of nickel at 50° to 60°, converts it into *n*-butyraldehyde, $CH_3.CH_2.CH_2.CHO$. Crotonic aldehyde combines with *two* molecules of sodium bisulphite instead of one. When the resulting addition compound is treated with acids, crotonic aldehyde is *not* regenerated, only one molecule of the bisulphite being eliminated. This shows that the second molecule of sodium bisulphite must have added at the double bond

QUESTIONS

1. Name the groups of organic compounds to which the substance having the molecular formula C_4H_8O may possibly belong. Give its possible constitutional formulae, and describe experiments which you would perform to determine its consitution *(Punjab, Inter. 1929)*

2. Give general methods of preparing aldehydes and the important reactions of the —HCO group. *(Punjab, B.Sc., Agr., 1930)*

[1] The Greek letter $\triangle$ *delta* is employed to represent a double bond ; the *position* of the double bond in a carbon chain is denoted by the number of first carbon atoms concerned in its formation

3. By what different methods may formaldehyde be synthesized? How does it react with (*i*) hydrogen cyanide, (*ii*) sodium bisulphite, (*iii*) phenylhydrazine, (*iv*) phosphorus pentachloride, and (*v*) sodium hydroxide? Write equations, and name the products obtained in each case.

4. Describe a method for the preparation of an aqueous solution of formaldehyde. State its important properties. Give equations. (*Unt. Prov. Inter., 1931*)

5. Explain the action of formaldehyde on each of the following: (*a*) ammoniacal silver nitrate, (*b*) hydroxylamine, and (*c*) phenylhydrazine. What part of the ormaldehyde molecule is each of these reactions due to? Show, by means of complete structural formulae, the relationship existing between formaldehyde, methyl alcohol, and methane.

6. How is formaldehyde prepared? In what important respects does it differ from acetaldehyde? Give its important uses.

7. Give the preparation and important properties of acetaldehyde. How can it be distingnished from formaldehyde and acetone?

(*East Punjab, Inter. 1948*)

8. Acetaldehyde may be regarded as a derivative of (*a*) ethane or (*b*) formaldehyde. Justify the statement by writing complete structural formulae for these compounds.

9. (*a*) Describe the preparation of *pure* acetaldehyde. How does it react with (*i*) ammonia, (*ii*) phenylhydraziae and, (*iii*) nascent hydrogen?

(*b*) What tests would you use to distinguish acetone from acetaldehyde?

(*Punjab, Inter., 1943*)

10. Give an account of the general methods by which aliphatic ketones can be prepared. What are their characteristic reactions?

How is acetone prepared commercially, and what are its uses?

(*Punjab, Inter., 1933*)

11 (*a*) Give the commercial preparation and uses of acetone. (*b*) Show what happens when acetone is—

(*i*) Reduced, (*ii*) Oxidized, (*iii*) Dehydrated, (*iv*) Treated with phosphorus pentachloride. (*Punjab, Inter., 1940*)

12. Compare and contrast the properties of aldehydes and ketones.

(*Punjab, Inter., 1919*)

13. Write complete structural formulae of acetone and propane, and deduce the structural relationship existing between the two.

14. Suppose you are given four liquids and told that amongst them you would find:—Methyl alcohol, ethyl alcohol, acetone and formalin. How would you proceed to discover which was which, and how would you determine their purity?

(*Unit. Prov., Inter., 1922*)

15. A solution contains either formaldehyde, ethyl alcohol, or acetone. How would you determine which of these compounds is present?

(*Punjab, Inter., 1923*)

16. A pleasant smelling organic liquid was found to contain C, 62·1%; H, 10·3%; and O, 27·6%. 0.22 gm. of the substance displaced, in Victor Meyer's apparatus, 84 ml. of air measured at N. T. P. With a concentrated solution of sodium bisulphite, the compound gave a colourless, crystaline product, but it failed to reduce ammoniacal silver nitrate solution. What was the substance?

(*Ans.* Acetone. $CH_3.CO.CH_3$.)

17. Explain the meaning of (*a*) polymerization, and (*b*) condensation, giving one illustration of each. (*Ajmer, Inter.*, 1932)

18. How will you convert acetaldehyde into crotonaldehyde? Write the structural formula of the latter compound, and discuss its chief chemical properties.

19. What test would you perform to distinguish between crotonaldehyde, acetaldehyde, formaldehyde, and acetone?

CHAPTER 13

MONOCARBOXYLIC ACIDS

1. General. The characteristic group present in the carboxylic acids is the **carboxyl group,** $-COOH$. These acids may be regarded as derived from the hydrocarbons, and represents the final stage in the oxidation of the methyl group of the hydrocarbon molecule, the intermediate stages being represented by primary alcohols and aldehydes The relationship between these compounds will be clear from the following examples :–

$H.CH_3$ Methane	$H.CH_2OH$ Methyl alcohol (methanol)	$H.CHO$ Formaldehyde (methanal)	$H.COOH$ Formic acid (Methane acid)
$CH_3.CH_3$ Ethane	$CH_3.CH_2OH$ Ethyl alcohol (ethanol)	$CH_3.CHO$ Acetaldehyde (ethanal)	$CH_3.COOH$ Acetic acid (ethane acid)

They are called **monocarboxylic acids, dicarboxylic acids**, etc., according to the number of carboxyl groups present in the molecule.

The monocarboxylic acids derived from the paraffin hydrocarbons are termed **fatty acids,** as the higher members of this series occur as the glyceryl esters in fats and oils. The names of the fatty acids all end in *-ic* and generally indicate their source of preparation, or the number of carbon atoms in the molecule. The Geneva names are derived from the parent hydrocarbons by the addition of the word "acid". The most important fatty acids are :

Acid	Parent Hydrocarbon
Formic acid, or Methane acid, $H.COOH$	Methane, CH_4
Acetic acid, or ethane acid, $CH_3.COOH$	Ethane, $CH_3.CH_3$
Propionic acid, or Propane acid, $C_2H_5.COOH$	Propane, $C_2H_5.CH_3$
Butyric acid, or Butane acid, $C_3H_7.COOH$	Butane, $C_3H_7.CH_3$
Palmitic acid, $C_{15}H_{31}.COOH$	Hexadecane, $C_{15}H_{31}.CH_3$
Stearic acid, $C_{17}H_{35}.COOH$	Octadecane, $C_{17}H_{35}.CH_3$

It should be noted that *each of the acids is derived from the corresponding hydrocarbon by the oxidation of a terminal methyl group to a carboxyl group.*

Acyl Groups. The groups which would remain on removing the hydroxyl from fatty acid molecules are termed "acyl" groups The name for each acyl group is derived from that of the corresponding acid by changing the termination *-ic* into *-yl* :

$H.CO-$, Foryml
$CH_3.CO-$, Acetyl
$C_2H_5.CO-$, Propionyl
$C_3H_7.CO-$, Butyryl.

2. General Methods of Formation. The following are the general methods for the preparation of carboxylic acids : —

(i) By the oxidation of the corresponding primary alcohol or aldehyde ; *e.g.*,

$$CH_3.CH_2OH \xrightarrow{-2H} CH_3.CHO \xrightarrow{+O} CH_3.COOH$$

Ethyl alcohol — Acetaldehyde — Acetic acid.

The oxidation can best be accomplished by means of potassium dichromate and sulphuric acid.

The reaction serves to show the **structural relationship** of primary alcohols, aldehydes and carboxylic acids

(2) By hydrolysing the alkyl cyanides by means of dilate acid or alkali, *e.g.*,

$$CH_3.C \equiv N + 3H.OH \rightarrow CH_3.C(OH)_2.OH + NH_3$$

Methyl cyanide — Ortho-acetic acid (unstable)

$$CH_3.C(OH)_2.OH \rightarrow CH_3.C(=O).OH + H_2O$$

Acetic acid

The reaction is of theoretical interest, as it elucidates the **structure of the carboxyl group.** The structural relationship between carboxylic acids and alkyl cyanides that this eaction establishes is expressed by the name acid nitriles given to alkyl cyanides. Thus, methyl cyanide is called aceto-nitrile and hydrogen cyanide formo-nitrile.

(3) By hydrolysing, by means of an alkali, a tribalogen derivative containing the three halogen atoms linked to the *same* carbon atom :

$$CHCl_3 + 3H.OH \rightarrow H.C(OH)_2.OH + 3HCl$$

Chloroform — Orthoformic acid (unstable)

$$H.C(OH)_2.OH \rightarrow H.C(=O).OH + H_2O$$

Formic acid

This reaction serves also to prove the **structure of the carboxyl group.**

(4) By the hydrolysis of esters. This method is specially helpful for preparing fatty acids from fats and oils.

3. Physical Properties. The lower fatty acids are colourless, corrosive liquids, possessing a strong, pungent odour. They distil without decomposition, and are readily soluble in water, the solutions showing an acid reaction. The members C_4 to C_9 are oily liquids sparingly soluble in water and possessing an unpleasant, rancid odour. From C_{10} upwards they are waxy solids, practically insoluble in water, but readily soluble in alcohol and ether; they can be distilled without decomposition only under reduced pressure, or in a current of steam

The following table summarizes certain physical constants of the more important fatty acids :

Acid	Formula	M. P. °C	B. P. °C	Sp. gr. at 25°
Formic	H. COOH	8·3	100·6	1·213
Acetic	$CH_3.COOH$	16·5	118	1·044
Propioic	C_2H_5COOH	—36	141	0·987
Butyric	$C_3H_7.COOH$.	—4	162	0·954
Palmitic	$C_{15}H_{31}.COOH$	62		—
Stearic	$C_{17}H_{35}.COOH$	69		—

Reactions. The molecule of a carboxylic acid, R.COOH, consists of two distinct parts, *viz.* (*i*) the alkyl group, and (*ii*) the carboxyl group. The general reactions of carboxylic acid may consequently be studied under three different heads:

(*a*) ***Reactions of the Alkyl Group.*** The alkyl group being the residue of the paraffin molecule, is stable towards most reagents (compare methane). Like the paraffin hydrocarbons, the fatty acids are acted on by chlorine in the presence of sunlight, or a halogen carrier (red phosphorus or iodine), yielding chloro-substituted acids.

Thus, acetic acid gives three **chloro-acetic acids.**

$$\underset{\text{Acetic acid}}{CH_3.COOH} + Cl_2 \rightarrow \underset{\text{Monochloroacetic acids}}{CH_2Cl\,COOH} + HCl$$

$$CH_2Cl.\,COOH + Cl_2 \rightarrow \underset{\text{Dichloroacetic acid}}{CHCl_2.COOH} + HCl$$

$$CHCl_2\,COOH + Cl_2 \rightarrow \underset{\text{Trichloroacetic acid}}{CCl_3.COOH} + HCl.$$

(*b*) ***Reactions of the Carboxyl Group.*** $-C\leqslant^{O}_{OH}$. The carboxyl group is responsible for the following two reactions that the carboxylic acids exhibit :—

(1) *Acidic Character.* When dissolved in water, the carboxylic acids undergo ionization, yielding hydrion :—

$$R.COOH \rightleftharpoons RCOO^- + H^+$$

Hence, these compounds show the typical behaviour of an acid: They neutralize alkalies, yielding **salts**, decompose carbonates with evolution of carbon dioxide, and attack metals, such as iron or zinc, yielding hydrogen. Thus, acetic acid possesses the following reactions:—

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \rightleftharpoons \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

$$2CH_3COOH + K_2CO_3 \rightarrow \underset{\text{Potassium acetate}}{2CH_3COOK} + H_2O + CO_2$$

$$2CH_3COOH + Zn \rightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

Further, the anhydrous acids react with alcohols yielding **esters**; *e.g.*,

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The reaction, being reversible, is best carried out in the presence of concentrated sulphuric acid, which serves to keep up the water produced in the reaction, and thus shifts the equilibrium towards the right ('Le Chatelier's principle). Thus a far better yield of ester is produced than it would be possible in the absence of a dehydrating agent.

(2) *Action of Phosphorus Pentachloride.* Since there is a *hydroxyl* group forming a part of the carboxyl group, the carboxylic acids react with phosphorus pentachloride (compare alcohols), yielding **acid chloride :**

$$\underset{\text{Acetic acid}}{CH_3C\leqslant^{O}_{OH}} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3C\leqslant^{O}_{Cl}} + POCl_3 + HCl$$

(*c*) ***Decompositions.*** Carboxylic acids and their salts undergo certain decompositions involving the carboxyl group or its residue in the molecule. Such reactions are detailed below:—

(1) When subjected to electrolysis, the carboxlic acids undergo decomposition, hydrogen being evolved at the cathode and a mixture of carbon dioxide and a *hydrocarbon* at the anode: *e. g.*,

$$\begin{matrix} CH_3COOH \\ | \\ CH_3COOH \\ \text{Acetic acid} \\ \text{(2 molecules)} \end{matrix} \xrightarrow{-} \underset{\text{Ethane}}{CH_3.CH_3} + 2CO_2 + H_2$$

(2) When an alkali salt of a fatty acid is heated with soda-lime, carbon dioxide is eliminated and a *hydrocarbon* is produced

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \rightarrow Na_2CO_3 + \underset{\text{Methane}}{CH_4}$$

(3) When ammonium salt of a carboxylic acid is distilled, an *amide* is produced :

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

If the ammonium salt or the amide be distilled with P_2O_5, a *nitrile* is produced :

$$CH_3CONH_2 \rightarrow \underset{\text{Acetonitrile}}{CH_3CN} + H_2O.$$

(4) When calcium salt of a fatty acid (other than formic) is subjected to dry distillation, a ketone is produced :

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \rightarrow \underset{\text{Acetone}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!=\!O} + CaCO_3$$

In the case of calcium formate, formaldehyde results : -

$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \rightarrow \underset{\text{Formaldehyde}}{H.C\!\leqslant\!\begin{matrix} H \\ O \end{matrix}} + CaCO_3.$$

4. Detection of the Carboxyl Group. The presence of the carboxyl group in a given substance can be detected as follows :

(1) If the substance is soluble in water, the solution will show the usual properties of hydrion. Thus, it will turn blue litmus red, and decompose sodium carbonate with the evolution of carbon dioxide.

(2) If insoluble in water, it should dissolve in a solution of sodium carbonate with the evolution of carbon dioxide, leaving no oily or solid residue.

(3) If the substance be distilled with soda-lime, and the residue treated with dilute hydrochloric acid, carbon dixide will be evolved.

5. Constitution of Carboxylic Acids. The constitution of the fatty acids follows from their synthesis from alkyl cyanides and trihalides (*p.* 135). When an alkyl cyanide, $R\,C \equiv N$, is heated with an alkali, or a dilute mineral acid, we get a molecule each of ammonia and a fatty acid. Since the acid produced has the same number of carbon atoms in the molecule as the alkyl cyanide, the carbon chain must have remained intact, the cleavage occurring at the $C\equiv N$ linkage. The hydrolysis may be explained by assuming the molecule of water to be sdlit into hydrogen and hydroxyl, the hydrogen atom, being electropositive in character, goes to the electronegative nitrogen atom, while the hydroxyl goes to the carbon. By a three-fold repetition of this

process, we would get a molecule each of ammonia and a trihydroxy compound containing the three hydroxyls linked to the same carbon atom :

$$RC{\equiv}N + 3H.OH \rightarrow RC(OH)_3 + H_3N$$

But since the acid produced is not $R.CO_3H_3$ but $R.CO_2H$ (*i.e.*, it contains one molecule of water less), we must assume that the trihydroxy compound, like most others containing more than one hydroxyels linked to the same carbon atom, at once loses a molecule of water as shown below :—

$$RC(OH)_3 \xrightarrow{-H_2O} R.C(=O)OH$$

Hence the acid obtained possesses the above structure, (*i.e.*, it contains a carboxyl group. $-C{\leqslant}^{O}_{OH}$.

The above view of the constitution of the carboxyl group is fully supported by the reactions of these acids. Thus the presence of a hydroxyl in the carboxyl group is proved by the action of phosphorus pentachloride, which gives rise to an acid chloride, $R.CO.Cl$. Further, the replacement by a metal, of only *one* of the hydrogen atoms present in the molecule shows that this one is in a different state of combination from the rest , *i.e* , the replaceable hydrogen atom forms a part of the carboxyl group.

6. Formic Acid, *Methane Acid*, $H.COOH$.

Occurrence. This acid occurs in ants (L. *formica*), stinging nettles, bees and wasps, and also in perspiration, urine and the juice of flesh, and may be obtained from these sources by distillation with water.

Formation. Formic acid may be prepared by the general methods described in Sec 122, though none of these is employed in actual practice for the preparation of this acid. These reactions are summarized below :

(1) *By Oxidation of Methyl Alcohol or Formaldehyde :—*

$$\underset{\text{Methyl alcohol}}{CH_3.OH} \xrightarrow{-2H} \underset{\text{Formaldehyde}}{H.CHO} \xrightarrow{+O} \underset{\text{Formic acid}}{H.COOH}$$

The oxidation can best be effected by means of potassium dichromate and sulphuric acid.

(2) *By Hydrolysis of Hydrogen Cyanide.* When hydrogen cyanide is treated with concentrated hydrochloric acid, it gets hydrolysed into formic acid and ammonia :

$$\underset{\text{Hydrogen cyanide}}{H.C{\equiv}N} + 3H.OH \rightarrow \underset{\text{Orthoformic acid (unstable)}}{H.C(OH)_3} + NH_3$$

$$H.C(OH)_3 \rightarrow H.C(=O)OH + H_2O$$

Formic acid

(3) *By Hydrolysis of Chloroform.* When chloroform is heated with alcoholic potash, it gets hydrolysed into formic acid and hydrochloric acid, a mixture of the potassium salts of these acids being produced (compare *p.* 107).

Laboratory Preparation. Formic acid may be prepared in the laboratory by heating oxalic acid crystals, $(COOH)_2.2H_2O$, with an equal weight of anhydrous glycerol in a flask connected to a condenser and a receiver. The temperature is maintained at 110°, until the evolution of carbon dioxide slackens. The contents of the flask are then allowed to cool somewhat, a further quantity of oxalic acid crystals is added, and the heating renewed, when an aqueous solution of formic acid distils over. The addition of oxalic acid crystals may be repeated a number of times, until the required quantity of formic acid has been obtained.

The reaction has been shown to occur in two stages :

In the *first stage*, the primary oxalic ester of glycerol is formed :

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + \begin{array}{l} COOH \\ | \\ COOH \\ \text{Oxalic acid} \end{array} \rightarrow \begin{array}{l} CH_2O\,CO.COOH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol mono-oxalate} \end{array} + H_2O$$

This, with the rise of temperature, loses a molecule of carbon dioxide, yielding glycerol monoformate :—

$$\begin{array}{l} CH_2O.CO.COOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \rightarrow \begin{array}{l} CH_2\,OOCH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol monoformate} \end{array} + CO_2$$

In the second stage, when more of oxalic acid crystals are added and the mixture reheated, glycerol monoformate is hydrolysed by the water of crystallization present in oxalic acid crystals, and formic acid is set free :

$$\begin{array}{l} CH_2.OOCH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + H.OH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH + HCOOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array}$$

While the formic acid distils over, the glycerol reacts with a further quantity of oxalic acid, yielding more of glycerol monoformate. The same cycle of changes is repeated on the addition of a fresh supply of oxalic acid crystals :—

Expt. 1. *Preparation of Formic Acid :—*

Glycerol, 30 ml.

Oxalic acid crystals, 60 gm.

Place the glycerol together with one-half (30 gm.) of the oxalic acid in a flask fitted with a thermometer and attached to a Liebig condenser (Fig. 1). Heat the flask on a sand-bath at a temperature of 110°. A vigorous evolution of carbon dioxide will occur ; when it slackens, allow the mixture to cool somewhat, add the remainder of the oxalic acid, and repeat the heating at 110°. The evolution of carbon dioxide will begin afresh, and, at the same time, aqueous formic acid will distil over.

Use the distillate obtained in this experiment for studying the reactions of formic acid (Expt. 2.)

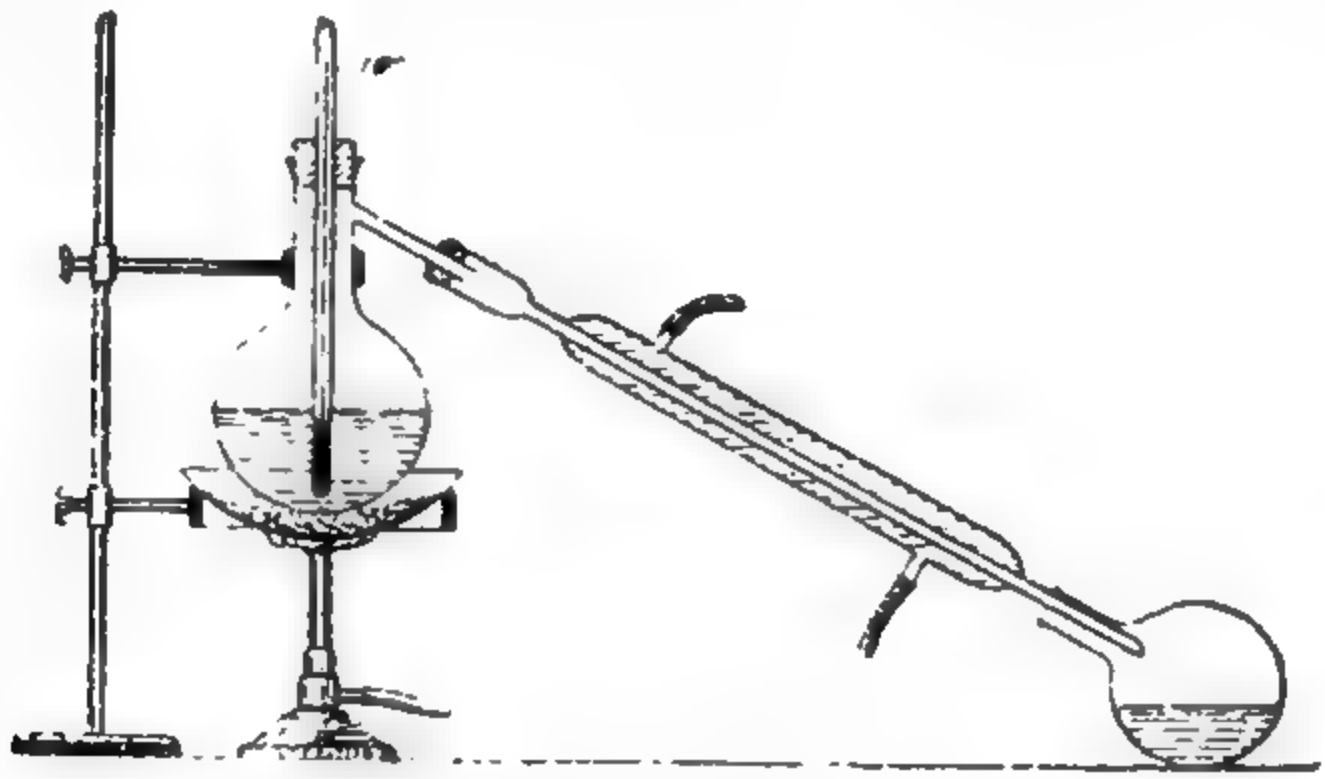


Fig. 1. Preparation of Formic Acid.

Preparation of Anhydrous Formic Acid. From the aqueous solution of formic acid, obtained as above, the anhydrous acid may be isolated as follows:—

(1) The distillate is heated nearly to boiling, and is neutralized with lead carbonate. The boiling liquid is then filtered through a Buchner funnel to remove the excess of lead carbonate. On allowing the filtrate to cool, needle-shaped crystals of lead formate are deposited. These are separated and dried by pressing between folds of filter paper.

(2) The crystals of lead formate are placed in a gently sloping glass tube, down which hydrogen sulphide is passed. The formic acid flows off at the lower end, and is collected.

$$(HCOO)_2Pb + H_2S \longrightarrow 2H.COOH + PbS$$

Lead formate — Formic acid

(3) The acid is freed from dissolved hydrogen sulphide by distilling it over a little lead formate.

Manufacture. Formic acid is manufactured by passing carbon monoxide at a pressure of 8 atmospheres over soda-lime heated to 210°.

$$CO + NaOH \longrightarrow H.COONa$$

The resulting sodium formate is distilled with sodium hydrogen sulphate, when anhydrous formic acid passes over.

$$HCOONa + NaHSO_4 \longrightarrow HCOOH + Na_2SO_4$$

Physical Properties. Anhydrous formic acid is a colourless liquid, possessing a penetrating, pungent odour, and boiling at 100·6°. It is strongly corrosive, and raises blisters on the skin. It is perfectly miscible with water, alcohol, ether and many other solvents.

Reactions. The reactions of formic acid, H.COOH, may be divided into three classes:—

(A) **Reactions of the Carboxyl Group** $-C\lessgtr^{O}_{OH}$.

1) *Acidic Character.* The hydrogen atom forming a part of the carboxyl group is ionizable. Hence formic acid, when in aqueous solution, yields hydrion:

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

The aqueous solution, therefore, possesses the usual properties of an acid : It has a sour taste, and turns blue litmus red. It neutralizes alkalies, yielding salts called **formates,** decomposes carbonates with the evolution of carbon dioxide, and attacks metals, such as zinc and iron producing hydrogen.

$$HCOOH + NaOH \rightleftharpoons \underset{\text{Sodium formate}}{HCOONa} + H_2O$$

$$2HCOOH + Na_2CO_3 \rightarrow 2HCOONa + H_2O + CO_2$$

$$2HCOOH + Zn \rightarrow \underset{\text{Zinc formate}}{(HCOO)_2Zn} + H_2$$

Anhydrous formic acid reacts with alcohols giving **esters** ; *e.g.*,

$$HCOOH + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl formate}}{HCOOC_2H_5} + H_2O$$

(2) *Reaction with Phosphorus Pentachloride.* Formic acid like other carboxylic acids, reacts with phosphorus pentachloride. But, as formyl chloride is too unstable to exist, we get in this case carbon monoxide and hydrogen chloride :-

$$\underset{\text{Formic acid}}{HCOOH} + PCl_5 \rightarrow \underset{\text{Formyl chloride}}{HCOCl} + POCl_3 + HCl$$

$$HCOCl \rightarrow HCl + CO$$

(*B*) **Reactions of the $-C\leqslant^{H}_{O}$ Group** (Reducing Properties). Formic acid, like the aldehydes, contains a $-C\leqslant^{H}_{O}$ group. For this reason, it acts as an active reducing agent. Thus, when a solution of silver nitrate is added to the acid, and the mixture heated, a precipitate of metallic silver is produced, the formic acid being oxidized to water and carbon monoxide :

$$HCOOH + O \rightarrow H_2O + CO_2$$

The reducing power of the acid may be employed **to distinguish formic acid from its homologues,** which, since they possess no aldehydic grouping, show no reducing properties.

(*C*) **Decomposition.** Formic acid is capable of undergoing decomposition in two different ways :—

(*i*) $HCOOH \rightarrow H_2O + CO$
(*ii*) $HCOOH \rightarrow H_2 + CO_2$

The decomposition (*i*) is brought about by warming the acid with concentrated sulphuric acid, or by passing its vapour over heated alumina. Finely-divided copper, nickel and certain other catalysts bring about the decomposition (*ii*).

Expt. 2, *Detection of Formic Acid.* In order to apply the following tests, the acid must be exactly neutralized with sodium carbonate and a few drops of ammonia, the excess of the latter being boiled off. A part of the solution should be evaporated to dryness to get the solid formate :—

(1) *Action of Heat.* On heating the sodium salt in a dry tube, hydrogen is set free and the residue gives the tests of an oxalate :

$$\underset{\text{Sodium formate (2 molecules)}}{\begin{matrix}HCOONa\\+\\HCOONa\end{matrix}} \rightarrow H_2 + \underset{\text{Sodium oxalate}}{\begin{matrix}COONa\\|\\COONa\end{matrix}}$$

(2) When the dry salt is heated with *dilute sulphuric acid*, pungent, penetrating odour of formic acid is evolved.

(3) With *concentrated sulphuric acid*, carbon monoxide is evolved, which may be ignited at the mouth of the test-tube (distinction from acetic acid).

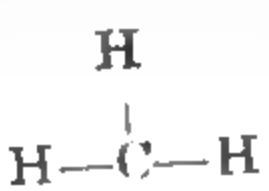
(4) When a solid formate is heated with *alcohol and concentrated sulphuric acid*, a pleasant, fruity odour of ethyl formate is obtained.

(5) *Ferric chloride*, when added to a neutral solution of a formate, gives a red coloration owing to the formation of ferric formate; on heating the solution a red-dish brown precipitate of a basic ferric formate is produced (compare acetic acid).

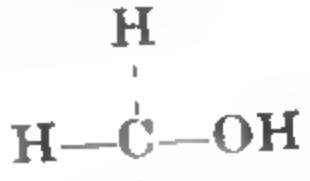
(6) *Silver nitrate*, when added to a neutral, concentrated solution of a formate, gives a white crystalline precipitate of silver formate. On standing the precipitate darkens, owing to reduction to metallic silver. In dilute solution there occurs no precipitation but on warming, separation of metallic silver takes place (distinction from acetic acid).

7. Constitution of Formic Acid. The structure of formic acid, $H.C\lessdot^{O}_{OH}$, follows from its synthesis from hydrogen cyanide, $H.C{\equiv}N$ (*p.* 173). This view is fully supported by its formation by the oxidation of formaldehyde, $H.C\lessdot^{O}_{H}$, and by the hydrolysis of chloroform (*p.* 107), and also by its various reactions.

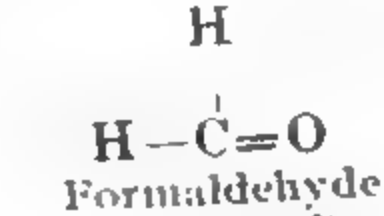
From the formula of formic acid it is evident that this compound is a **derivative of methane**: hence the name *methane acid*. Its structural relationship with methane, methyl alcohol, formaldehyde, and formonitrile is shown below:—



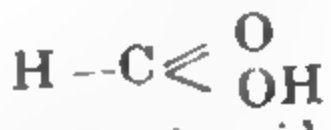
Methane



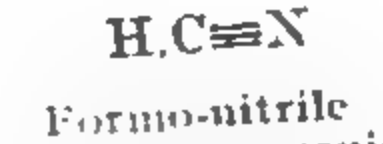
Methyl alcohol
(Methanol)



Formaldehyde
(Methanal)



Formic acid
(Methane acid)



Formo-nitrile
(Hydrogen cyanide)

Uses. 1. Because of its strong germicidal action, formic acid is used in the tanning and brewing industries.

2. It finds an extensive application in the textile industry as an acid for the dye baths.

8. Acetic Acid, *Ethane Acid*, CH_3COOH. This is one of the most common organic acids, and the one longest known. In fact dilute acetic acid in the form of **vinegar** was the only acid known to the ancients.

Formation. Acetic acid may be obtained by the oxidation of ethyl alcohol or acetaldehyde, or by the hydrolysis of methyl cyanide (*p.* 168).

9. Manufacture of Acetic Acid. Acetic acid is manufactured by three different processes:—

(1) **Quick Vinegar Process.** Larger quantities of dilute acetic acid or **vinegar** are obtained from dilute alcohol, wine, beer, etc., by oxidation with atmospheric oxygen under the catalytic action of bacteria, chiefly **bacterium aceti** (Fig. 3). The optimum temperature for the reaction is 30°.

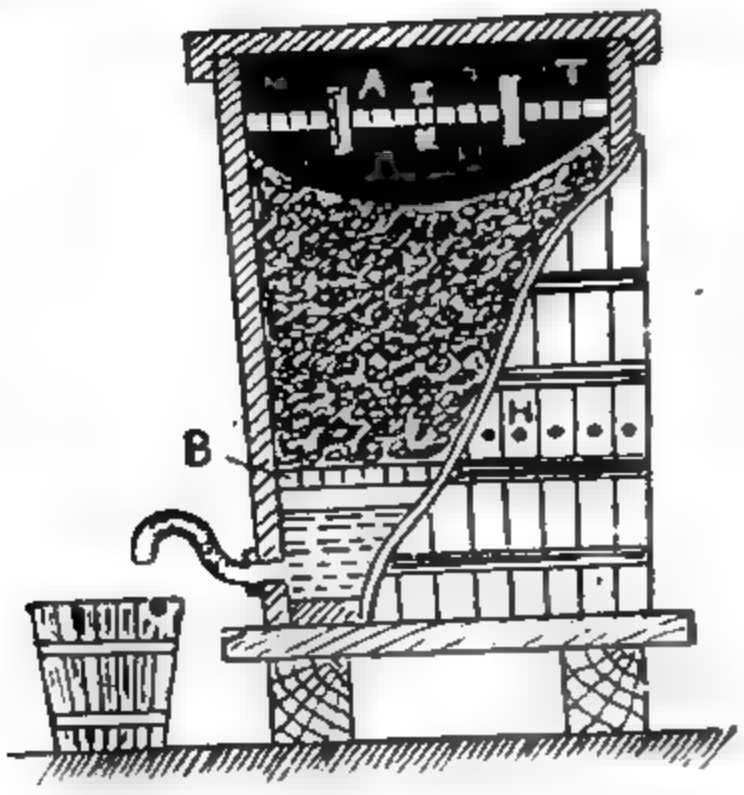


Fig. 2.

In the "quick" process of the preparation of vinegar, large wooden vats (Fig. 2) are filled with beech-wood shavings moistened with strong vinegar, containing *bacterium aceti* (Fig. 3). Dilute alcohol (6 to 10 per cent.) is allowed to flow slowly through the vats. The shavings serve firstly to present a large liquid surface to the oxidizing action of air, and secondly, they provide a suitable feeding-ground for the acetic bacteria. Each vat is provided with a perforated top, *T*, and a perforated false bootom, *B*. Holes, *H* in the side of the vat near the bottom serve to admit an ascending current of air, opposite in direction to the flow of the liquid. The process is repeated several times to complete the oxidation, which requires about a fortnight. The vinegar obtained contains about 6 to 7 per cent of acetic acid.

(2) ***From Wood Distillation.*** Large quantities of acetic acid are obtained from pyroligneous acid (*p.* 118). This is separated from the wood-tar and redistilled. The vapours are passed through hot milk of lime, which retains acetic acid as calcium acetate, while acetone and methyl alcohol vapours pass on the condenser.

Fig. 3. Acetic Acid Bacteria (as seen under the microscope)

The calcium acetate solution, obtained as above, is filtered and concentrated to obtain crystals of the crude salt. These are dried and carefully heated at 250° to decompose tarry impurities. The residual "*grey acetate of lime*," as it is commercially called, is distilled with the required quantity of concentrated hydrochloric acid, whereby dilute acetic acid of about 40 per cent strength is obtained. This is mixed with a little potassium permanganate to oxidize the impurities, and then redistilled.

To obtain nearly anhydrous acid the distillate is neutralized with sodium carbonate, and the solution concentrated to get crystals of sodium acetate, $CH_3COONa\,3H_2O$. These are fused to expel water, and the anhydrous salt is then distilled with concentated sulphuric acid. The distillate is strong enough to freeze readily in cold weather, and is known as **glacial acetic acid**.

(3) ***From Calcium Carbide.*** A method of manufacture, which was developed during the Great War, is from calcium carbide, *via* acetylene and acetaldehyde (*p.* 90). The latter compound is oxidized to acetic acid by air under pressure in the presence of vanadium and cerium oxides.

10. Properties of Acetic Acid. Acetic acid is a colourless liquid, having a very strong, pungent odour and corrosive action on it skin. In the cold weather, the acid freezes to give a transparent, crystalline mass (m.p. 16·6°). Hence the name glacial acetic acid given to the anhydrous acid. The pure acid boils at 118°, and is heavier than water.

Reactions. The reactions of acetic acid, like those of other acids

of this series, may be divided into *three* groups:—

(*a*) *Reactions of the Methyl Group.* Since acetic acid, CH_3COOH, contains a methane residue. (*i.e.*, the methyl group,—CH_3), it reacts with chlorine in the presence of sunlight, or a halogen carrier, giving **chloro-acetic acids**. (*p* 169). Like methane, acetic acid is stable towards oxidizing agents, and *shows no reducing properties* (distinction from formic acid). Other acids of this series resemble acetic acid in this respect.

(*b*) *Reactions of the Carboxyl Group.* (See *p.* 136).

(*c*) *Decomposition* (See *p.* 136).

Detection. Acetic acid and its salts may be identified as in the following experiment.

Expt. 3 *Detection of Acetic Acid and Acetates.* The free acid may be identified by its characteristic, pungent smell. For the following tests, prepare a *neutral* solution as in the case of formic acid (Expt. 2), and evaporate a part of it to get solid sodium acetate.

(1) Heat the dry sodium salt in a test-tube: no gas is evolved (distinction from formic acid).

(2) Heat the dry salt with sulphuric acid (dilute or concentrated); pungent smelling vapour of acetic acid is evolved.

(3) Heat the dry salt with ethyl alcohol and concentrated sulphuric acid; a fruity odour of ethyl acetate is evolved.

(4) Add ferric chloride to the *neutral* solution: a deep red coloration, owing to the formation of ferric acetate, is developed. The colour is discharged on boiling the liquid, a brownish red precipitate of basic ferric acetate being deposited. The cold liquid also gets decolorized on the addition of hydrochloric acid owing to the decomposition of ferric acetate

11. Uses of Acetic Acid. (1) In the form of vinegar, acetic acid is much used as a condiment and for pickling.

(2) In the laboratory, the acid is used as a reagent and a solvent.

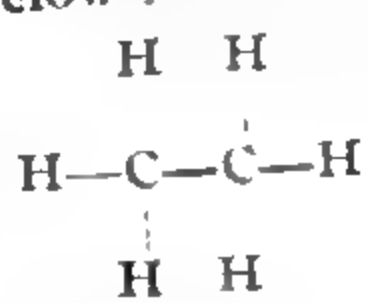
(3) Large quantities of this acid are used in the manufacture of dyes, rayon and paper

(4) It is also employed on a large scale in the manufacture of ethyl acetate, amyl acetate and other esters for use as solvents in the lacquer industry.

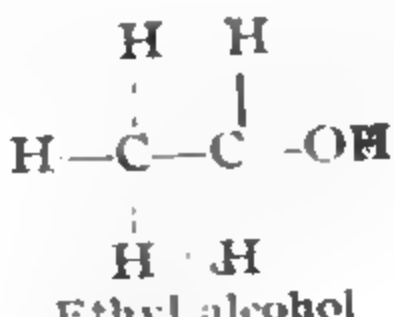
(5) Certain metallic acetates (*viz.*, of lead, copper, aluminium and iron) are used on a large scale (*see* below).

12. Constitution of Acetic Acid. The structure of acetic acid, $CH_3.C\leqslant^{O}_{OH}$, follows from its formation by the hydrolysis of methyl cyanide, and by the oxidation of acetaldehyde. It is fully supported by its various reactions.

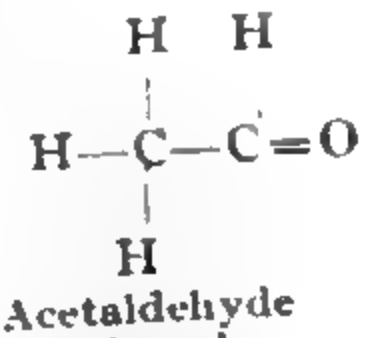
Since the acid contains two carbon atoms in the molecule, it is evidently a derivative of ethane; hence the name **ethane acid**. Its structural relationship with ethane ethyl alcohol, aldehyde and aceto-metrile is shown below :—



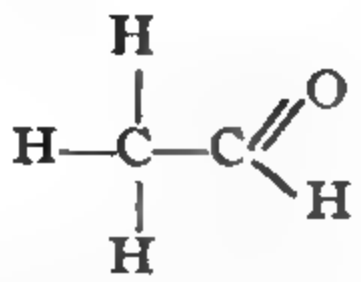
Ethane



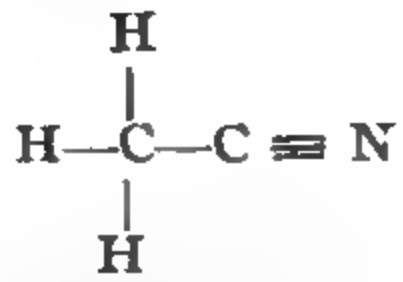
Ethyl alcohol
(Ethnol)



Acetaldehyde
(Ethanal)



Acetic acid
(Ethane acid)



Acetonitrile
(Methyl cyanide)

13. Acetates. All normal acetates are soluble in water, some basic acetates are insoluble.

Sodium acetate, $CH_3COONa.3H_2O$ is used for artificial cooling and as a reagent. When heated with soda lime it yields methane.

$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$$

Lead acetate or *sugar of lead*, $(CH_3COO)_2Pb.3H_2O$, and *basic lead acetate*, $CH_3COOPb.OH$, are used in the manufacture of lead preparations (*e.g.*, "white lead".) An aqueous solution of lead acetate is sometimes used under the name "lead lotion" as an external application in cases of sprains, etc.

Basic copper acetate, $CH_3COO.CuOH$, technically known as **verdigris,** is used in the manufacture of green paint. Normal acetates of *aluminium*, *chromium*, *iron* and *copper* are employed as mordants.

14. Distinction between Formic Acid and Acetic Acid. The following reactions distinguish formic acid from acetic acid:—

(1) *Reducing Action.* Formic acid is an active reducing agent (*p.* 141); acetic acid, since it contains no hydrogen atom directly linked to the >CO group, possesses no reducing property.

(2) *Decomposition.* Formic acid undergoes decomposition when heated in the presence of catalysts, such as finely-divided copper or nickel,

$$HCOOH \longrightarrow H_2 + CO_2$$

When heated with concentrated sulphuric acid, it yields carbon monoxide:—

$$HCOOH \longrightarrow H_2O + CO$$

Acetic acid is quite stable under these conditions.

(3) *Action of Heat on Alkali Salts.* When an alkali salt of formic acid is heated, it yields hydrogen,

$$2HCOONa \rightarrow H_2 + \begin{matrix} COONa \\ | \\ COONa \end{matrix}$$

Sodium formate — Sodium oxalate

Alkali salts of acetic acid are *not* decomposed when heated alone; when heated with soda-lime, they give methane,

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \rightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3.$$

(4) *Action of Heat on Calcium Salts.* When calcium formate is heated, it gives formaldehyde,

$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \rightarrow \underset{\text{Formaldehyde}}{H.C\leqslant \begin{matrix} H \\ O \end{matrix}} + CaCO_3$$

Calcium acetate on similar treatment yields acetone,

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \longrightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3} + CaCO_3$$

15. Butyric Acid, *Butane Acid*, $CH_3.CH_2.CH_2.COOH$. This acid occurs as the glyceryl ester in butter to the extent of about 7 per cent, and in the free state in perspiration.

The acid is prepared by the **butyric fermentation** of saccharine or starchy materials. The fermentation is effected by the combined action of the *lactic bacilli* and the *butyric bacilli*. The latter consist of slender rods in active movement.

A solution of starch or glucose is prepared, and to this some sour milk (which contains lactic ferment) and putrid cheese (which contains butyric ferment) are added. Some chalk or zinc carbonate is also added to keep down the hydrion concentration of the fermenting liquid (as excessive acidity is ruinous to the growth of the ferments) and also a little tartaric acid, ammonium phosphate, and magnesium sulphate, in order to stimulate the growth of the ferments. The butyric acid, as soon as produced, is neutralized by the calcium or zinc carbonate present. The resulting solution, containing calcium or zinc butyrate, is filtered, evaporated, decomposed with hydrochloric acid, and butyric acid separated by distillation.

During the above process of fermentation, the starch is first converted into glucose. The latter then undergoes lactic fermentation (*q.v.*) : and finally the lactic acid is decomposed into butyric acid

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow 2\underset{\text{Lactic acid}}{C_3H_6O_3} \rightarrow \underset{\text{Butyric acid}}{C_4H_8O_2} + 2CO_2 + 2H_2$$

Butyric acid is an oily liquid (b. p. 163°), having an unpleasant smell of rancid butter. It is used in the manufacture of esters.

16. Palmitic Acid, $C_{15}H_{31}COOH$, **and Stearic Acid,** $C_{17}H_{35}.COOH$, are higher members of the acetic acid series. They are found as glyceryl esters in fats and oils, from which source they are obtained by hydrolysis with superheated steam in the presence of lime, the latter acting as a catalyst:—

$$\begin{array}{l} C_{15}H_{31}COO.CH_2 \\ | \\ C_{15}H_{31}COO.CH \\ | \\ C_{15}H_{31}COO.CH_2 \\ \text{Glyceryl tripalmitate} \\ \text{(tripalmitin)} \end{array} + 3H.OH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3\underset{\text{Palmitic acid}}{C_{15}H_{31}.COOH}$$

$$\begin{array}{l} C_{17}H_{35}COO.CH_2 \\ | \\ C_{17}H_{35}COO.CH \\ | \\ C_{17}H_{35}COO.CH_2 \\ \text{Glyceryl tristearate} \\ \text{(tristearine)} \end{array} + 3H.OH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3\underset{\text{Stearic acid}}{C_{17}H_{35}.COOH}$$

Both the acids are colourless, waxy solids almost insoluble in water. The former acid melts at 62° and the latter at 69°. In their chemical behaviour, these acids resemble the other members of the series and give rise to salts and esters.

A mixture of the two acids, obtained by hydrolysing fats and oils and called **stearine**, is used in the manufacture of "Stearine" candles. Soap is a mixture of the sodium salts of these acids.

17. Oleic Acid, $C_{17}H_{33}.COOH$, is an *unsaturated* acid containing a double bond in the molecule. It is given the structure :

$$CH_3.(CH_2)_7CH{:}CH.(CH_2)_7COOH$$

The glyceryl ester of oleic acid is present in fats and oils together with stearine and olein. When fats and oils are submitted to hydrolysis by means of superheated steam, oleic acid is obtained together with palmitic and stearic acids,

$$\begin{array}{l} C_{17}H_{33}COO.CH_2 \\ | \\ C_{17}H_{33}COO.CH \\ | \\ C_{17}H_{33}COO.CH_2 \end{array} + 3H.OH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\text{Oleic acid}}{3C_{17}H_{33}COOH}$$

Glyceryl trioleate (triolein) — Glycerol

The resulting mixture of acids is allowed to cool in shallow trays, when palmitic and stearic acids crystallize out. The cakes of fatty acids thus obtained are wrapped in filter cloth and pressed in a hydraulic press. The oleic acid, being a liquid, flows out into a receptacle placed beneath the press. The solid cake remaining behind the cloth consists of a mixture of palmitic and stearic acids and is used in making stearine candles.

Oleic acid is a colourless liquid at the ordinary temperature. When cooled, it soldifies at 4°C., yielding a mass of colourless needles.

Oleic acid differs from the acids of the acetic series in being unsaturated. When treated with hydrogen in the presence of finely-divided nickel (*hydrogenation*), it gives stearic acid,

$$\underset{\text{Oleic acid}}{C_{17}H_{33}.COOH} + H_2 \rightarrow \underset{\text{Stearic acid}}{C_{17}H_{35}.COOH}$$

It also combines directly with a molecule of chlorine or bromine (compare ethylene).

Oleic acid is used as a wool oil and in soap manufacture.

QUESTIONS

1. Give general methods of formation and important reactions of fatty acids. How would you convert a fatty acid into (*a*) a paraffin (*b*) an aldehyde, and (*c*) a ketone? *(Punjab, B. Sc. Agr., 1934)*

2. Give the reasoning by which we have determined the constitution of the carboxyl group. Describe the chief methods by which a carboxyl group may be removed from or added to an organic compound. *(Punjab, Inter., 1914)*

3. Describe a method for preparing formic acid, and compare its properties with those of acetic acid. *(Ajmer, Inter., 1930)*

4. How can a pure, anhydrous sample of formic acid be prepared in the laboratory? In what important respects does it differ from its homologues? *(Unit. Prov. Inter., 1925)*

5. You are given the product of the distillation of wood. Describe how a specimen of pure acetic acid could be obtained from it. *(Punjab Inter., 1926)*

6. "Formic acid as a derivative of methane." Justify the statement. Show how it may be obtained from methane and converted back into that hydrocarbon.

7. How is ordinary vinegar manufactured? How would you prepare from it (*a*) glacial acid, (*b*) marsh gas, (*c*) acetone? *(Unit. Prov. Inter., 1920)*

8. Describe the reactions by which a fatty acid may be converted into paraffin, an aldehyde and a ketone. *(Punjab. Inter., 1931)*

9. Write structural formulæ to bring out the structural relationship between acetic acid, acetaldehyde, ethyl alcohol, and ethane. How could acetic acid be obtained from ethane and converted into this hydrocarbon?

10. Write structural formulæ of palmitic, stearic and oleic acids. How are these acids obtained on a commercial scale and to what uses are they put? In what way does oleic acid differ from stearic acid and how may it be converted into the latter compound?

CHAPTER 14

ACID CHLORIDES, ANHYDRIDES, AMIDES AND NITRILES

1. Acid Chlorides. Acid chlorides or **acyl chlorides** are derived from carboxylic acids by the replacement of the hydroxyl part of the carboxyl group by a chlorine atom, and consequently contain the group—COCl.

Acid	Acid Chloride
Formic acid, H. COOH	Formyl chloride, H.COCl
Acetic acid, CH_3. COOH	Acetyl chloride, CH_3.COCl
Propionic acid, C_2H_5.COOH	Propionyl chloride, C_2H_5.COCl

We shall describe acetyl chloride as a typical example of acid chloride.

2. Acetyl Chloride, CH_3COCl.

Preparation. Acetyl chloride is prepared by dropping phosphorus trichloride into glacial acid :

$$3CH_3COOH + 2PCl_3 \longrightarrow 3CH_3COCl + P_2O_3 + 3HCl.$$

Expt. 1. *Preparation of Acetyl Chloride.* 50 grams of glacial acetic acid are placed in a distillation flask, provided with a dropping funnel, a condenser and a receiver (fig. 1)). The side tube of the receiver is provided with a calcium chloride tube to keep out the moist air. 38 grams of phosphorus trichloride are gradually run

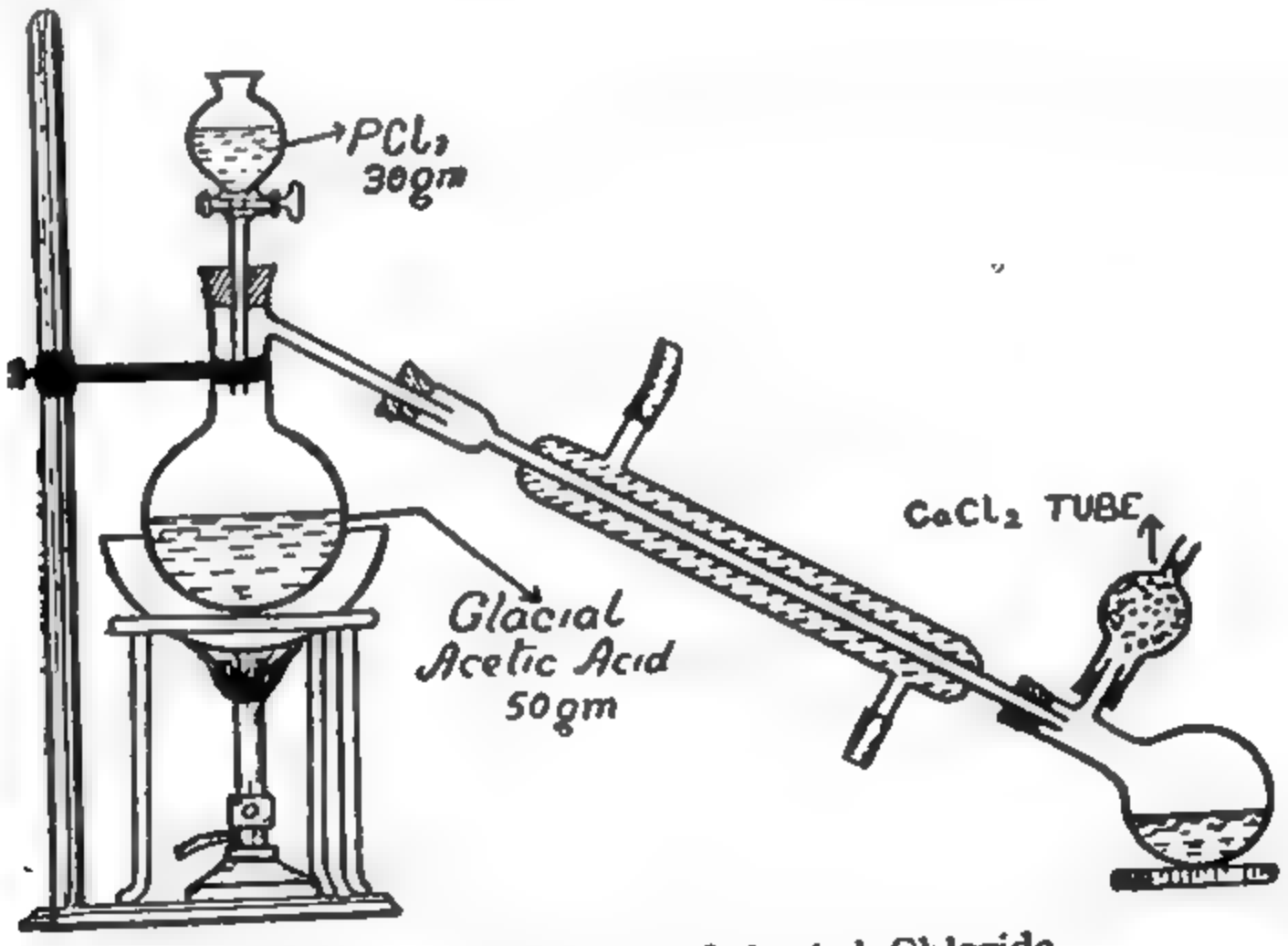


Fig 1. Preparation of Acetyl Chloride.

from the dropping funnel into the distilling flask. During the addition of the trichloride, the flask is cooled by immersion in cold water contained in the water bath. The temperature of the bath is then raised to 40°—50°, and kept at this point until the evolution of hydrogen chloride has slackened, and the liquid in the flask has separated into two layers. The water of the bath is then boiled, until no more liquid collects in the receiver.

PURIFICATION. The acetyl chloride is purified by redistillation from the flask used as the receiver during the preparation, the neck of the flask being provided

with a thermometer. The distillate is collected in another distillation flask, provided with a calcium chloride tube as before. The fraction passing between 55° and 56° is collected separately, and may be taken to be fairly pure for the ordinary laboratory work. Further purification, if desired, can only be effected by repeated fractional distillation.

Properties. (1) Acetyl chloride is a colourless, mobile liquid with a pungent odour. It boils at 55°.

(2) *Action of Water.* It is readily attacked by water, when acetic acid and hydrogen chloride are both produced :

$$CH_3COCl + H.OH \rightarrow CH_3COOH + HCl$$

(3) *Reaction with Alcohols.* Acetyl chloride reacts with alcohols, yielding esters ; *e.g.*,

$$\underset{}{CH_3COCl} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightarrow \underset{\text{Ethyl-acetate}}{CH_3COOC_2H_5} + HCl$$

(4) *Reaction with Ammonia.* When treated with ammonia, acetyl chloride yields acetamide:

$$CH_3COCl + NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$

The excess of ammonia used in the reaction, reacting on hydrogen chloride, first produced, forms ammonium chloride :

$$NH_3 + HCl \rightarrow NH_4Cl$$

(5) *Reduction.* When reduced by means of hydrogen in the presence of platinized barium sulphate (Rosenmund's reaction), acetyl chloride yields acetaldehyde : —

$$CH_3COCl + H_2 \rightarrow CH_3CHO + HCl$$

Constitution. The constitution of acetyl chloride is proved by (*i*) its formation from acetic acid by the action of phosphorus trichloride, and (*ii*) its reconversion into acetic acid by the action of water. It is fully supported by all the reactions of the compound.

3. Acetyl Chloride as a Reagent. Acetyl chloride is an important reagent, and is put to the following uses in the laboratory ;

(1) *Detection of the Hydroxyl Group.* Acetyl chloride is employed for detecting the presence of a hydroxyl group in the molecule of a compound. For this purpose, the substance, after being carefully dried, is added to an excess of acetyl chloride the mixture is heated under a reflux condenser for some time, and the unchanged acetyl chloride is then distilled off. If the substance contains no hydroxyl group, it will be recovered unchanged. If, on the other hand, it contains a hydroxyl group, an acetyl derivative will be formed :—

$$\underset{\text{Hydroxyl compound}}{R.OH} + CH_3COCl \rightarrow \underset{\text{Acetyl derivative}}{R.O\,CO.CH_3} + HCl$$

The formation of acetyl derivative will be indicated by the evolution of hydrogen chloride during the reaction ; or the product may be boiled with alcoholic sodium hydroxide and the resulting solution tested for an acetate :—

$$RO.CO.CH_3 + NaOH \rightarrow ROH + CH_3COONa$$

(2) *Determination of the Number of Hydroxyl Groups in a Compound.* This consists in the preparation of the acetyl derivatives as described above, and then analysing the acetyl derivative for the number of acetyl groups that it contains.

(3) *As a Synthetic Agent.* Acetyl chloride is employed for synthesizing acetic anhydride, acetamide, etc.

4. Acid Anhydrides. Acid anhydrides are derived from carboxylic acids by the removal of a molecule of water between two molecules of the acid ; *e.g.*,

$$\begin{matrix} CH_3COO\,H \\ CH_3CO\,OH \end{matrix} \xrightarrow{-H_2O} \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!>\!O$$

Acetic acid (2 molecules) → Acetic anhydride (1 molecule)

5. Acetic Anhydride, $\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!>\!O$.

Preparation. Acetic anhydride is obtained by the interaction of anhydrous sodium acetate and acetyl chloride :—

$$\begin{matrix} CH_3CO\,Cl \\ + \\ CH_3COO\,Na \end{matrix} \longrightarrow \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!>\!O + NaCl$$

Acetic anhydride

Expt. 2. *Preparation of Acetic Anhydride :*
Anhydrous sodium acetate, 50 gm.
Acetyl chloride, 30 c c

Fit up the apparatus shown in Fig 2, the side-tube of the receiver being connected to a calcium chloride tube to keep out atmospheric moisture. Place the anhydrous, finely powdered sodium acetate into the retort and drop slowly the acetyl chloride. When the whole of acetyl chloride has been added, remove the dropping

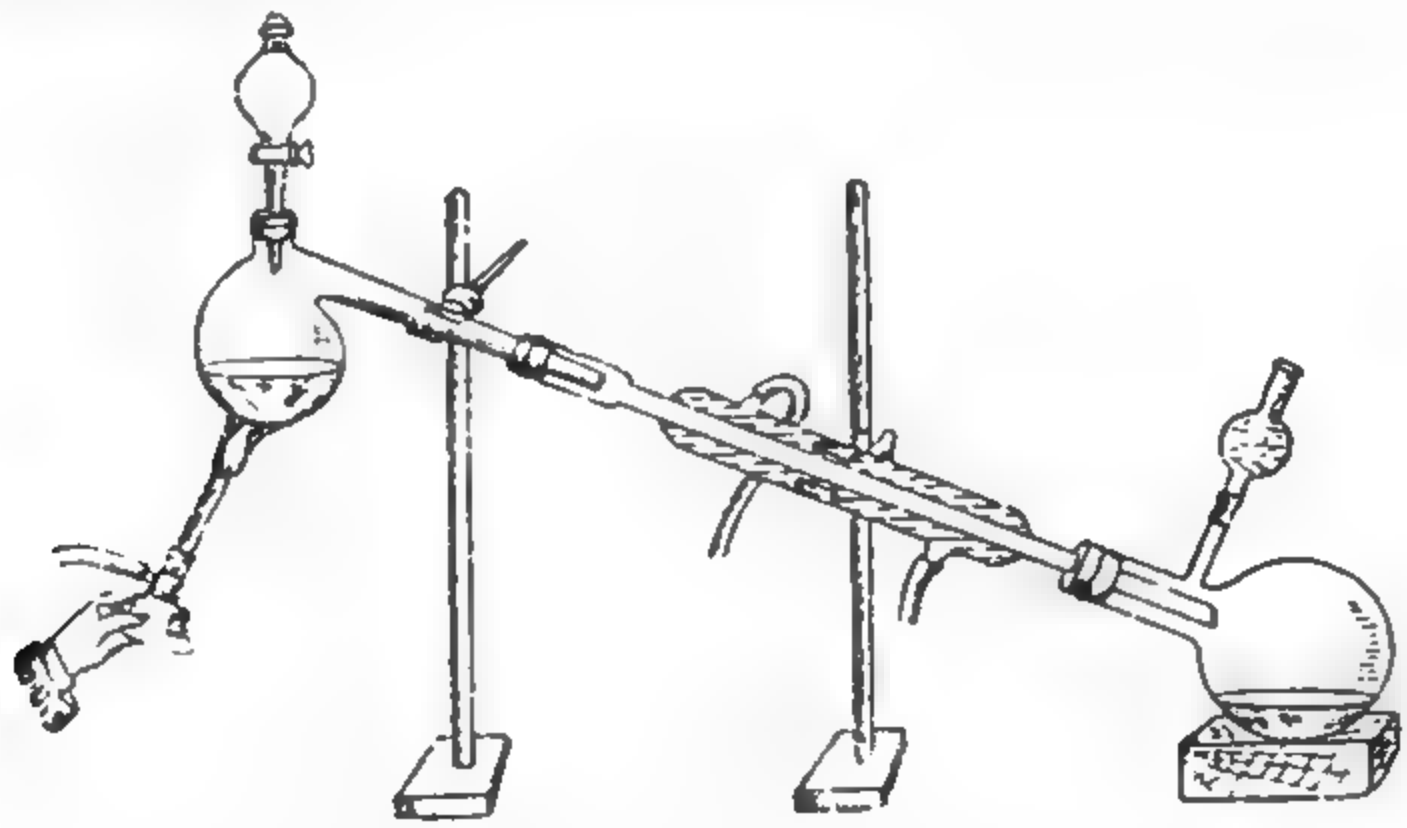


Fig. 2. Preparation of Acetic Anhydride.

funnel, stir the mixture well with a glass rod, and close the retort with a glass stopper. Heat the retort with a luminous flame kept in constant motion. When no more liquid collects in the receiver, add a little anhydrous sodium acetate to the collecting flask and redistil, collecting the fraction passing at 135° to 140°.

Physical Properties. Acetic anhydride is a colourless, non-fuming liquid having a pungent, acetic acid like odour. It boils at 137°, and is heavier than water.

Reactions. Like acetyl chloride, acetic anhydride reacts with water, alcohols, and ammonia, yielding the same products, though in each case the reaction does not occur so vigorously as with acetyl

chloride. These reactions are summarized in the following scheme :—

$$CH_3CO\,O.CO.CH_3 \text{ (Acetic anhydride)}$$
$$+$$

(1) $$HO\,H \xrightarrow{\text{water}} \underset{\text{Acetic acid}}{CH_3.COOH} + \underset{\text{Acetic acid}}{CH_3COOH}$$

(2) $$RO\,H \xrightarrow{\text{alcohols}} \underset{\text{Alkyl acetate}}{CH_3.CO.OR} + CH_3COOH$$

(3) $$NH_2\,H \xrightarrow{\text{ammonia}} \underset{\text{Acetamide}}{CH_3CO.NH_2} + CH_3COOH$$

In reaction (3) an excess of ammonia is used, and ammonium acetate is formed instead of free acetic acid as the by-product.

From the above equations, it is evident that only one of the two acetyl groups of acetic anhydride is used up in acetylation, the other being eliminated as acetic acid.

Constitution. The constitution of acetic anhydride is proved by (*i*) its formation by the interaction of acetyl chloride and sodium acetate and (*ii*) its conversion into acetic acid by the action of water.

Use as a Reagent. Like acetyl chloride, acetic anhydride is a valuable reagent for introducing acetyl groups into alcohols, sugars, ammonia, amines, and other organic substances.

6. Acid Amides. Acid amides are derived from the carboxylic acids by the replacement of the hydroxyl part of the carboxylic group by an $-NH_2$ group.

Acid	Amide
Formic acid, H.COOH	Formamide, $H\,CONH_2$
Acetic acid, CH_3.COOH	Acetamide, $CH_3.CO\,NH_2$
Propionic acid, C_2H_5.COOH	Propionamide, $C_2H_5\,CO\,NH_2$

We shall discuss acetamide as a typical example of this class of compounds.

7. Acetamide, $CH_3.CONH_2$.

Preparation. Acetamide may be obtained by the following methods :—

(1) By the action of acetyl chloride on ammonia,

$$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$$

(2) By the prolonged action of heat on ammonium acetate,

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

This is the usual laboratory method, the procedure being as follows :

Expt. 3. *Preparation of Acetamide from Ammonium Acetate.* Ammonium acetate (50 gm.) is boiled with an equal weight of glacial acetic acid in a large size flask, provided with a reflux condenser, for about 6 hours, and the reaction mixture is then rapidly distilled.

The distillate is fractionated, and the fraction passing above 200° is collected separately. This fraction solidifies on cooling, owing to the formation of a mass of

crystals of acetamide. The crystals are pressed between folds of filter paper so as to dry them.

(3) By the action of ammonia on ethyl acetate (or methyl acetate) :—

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + C_2H_5OH$$

Expt. 4. *Preparation of Acetamide from Ethyl Acetate.* The ester is left in contact with an equal volume of strong, aqueous ammonia, until it has dissolved. The solution is distilled slowly, the fraction passing above 200° being collected separately This fraction sclidifies on cooling. The crystals of acetamide thus obtained are dried by pressing between folds of filter paper.

Physical Properties. Acetamide is a colourless, crystalline solid. It melts at 82° and boils at 222°. It is readily soluble in water and alcohol.

Reactions. (1) When heated with a dilute alkali or a dilute mineral acid, acetamide gets hydrolysed into acetic acid and ammonia :

$$CH_3CONH_2 + H.OH \rightarrow CH_3COOH + NH_3$$

Expt. 5. (*i*) Warm a few crystals of acetamide with sodium hydroxide solution. Test the evolved ammonia with a moist red litmus paper.

(*ii*) Repeat the experiment, using dilute sulphuric acid instead of sodium hydroxide. Notice the smell of vinegar.

(2) When treated with nitrous acid (sodium nitrite and hydrochloric acid), it gives acetic acid, free nitrogen and water :

$$\left.\begin{matrix} CH_3CONH_2 \\ \vdots \\ +HONO \end{matrix}\right\} \rightarrow CH_3COOH + N_2 + H_2O$$

Expt. 6. Dissolve some acetamide in dilute hydrochloric acid and then add a dilute solution of sodium nitrite. Notice the evolution of nitrogen.

(3) When distilled with phosphorus pentoxide, acetamide gives methyl cyanide or acetonitrile : —

$$CH_3CONH_2 \rightarrow \underset{\text{Acetonitrile}}{CH_3CN} + H_2O$$

The reaction serves to show the structural relationship between acetic acid, acetamide and acetonitrile :—

(4) **Hofmann's Bromamide Reaction.** When acetamide is treated with bromine and aqueous potassium hydroxide, it yields methylamine :—

$$(i) \quad \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{\text{Acetobromamide}}{CH_3CONHBr}$$

$$(ii) \quad \left.\begin{matrix} CH_3CONHBr \\ + \\ HOH \end{matrix}\right\} \xrightarrow{KOH} \underset{\text{Methylamine}}{CH_3.NH_2} + HBr + CO_2$$

The above reaction may be employed (*a*) for the preparation of methylamine, and (*b*) for **descending a homologous series.** Thus, acetic acid, a derivative of ethane, may, by the help of this reaction, be converted into methylamine or into methyl alcohol[1], which are both derivatives of methane.

Constitution. The constitution of acetamide is proved (*i*) by its formation by the interaction of acetyl chloride and ammonia, (*ii*) by its various reactions.

8. Acid Nitriles. Acid nitriles, R C≡N, are derived from carboxylic

[1] Methyl alcohol is obtained from methylamine by the action of nitrous acid.

acids by the replacement of the carboxyl group by the —CN group. They may also be regarded as derived from hydrogen cyanide, **HCN**, by the replacement of the hydrogen atom by alkyl groups, hence the name alkyl cyanides.

Acid	Nitrile
Formic acid, H.COOH	Formo-nitrile, or Hydrogen cyanide, HCN
Acetic acid CH_3COOH	Aceto-nitrile, or methyl cyanide, CH_3CN
Propionic acid, C_2H_5COOH	Propiono-nitrile, or ethyl cyanide, C_2H_5CN

Formation. Acid nitriles may be prepared by the following general methods :—

(1) *From amides*, by distilling the latter with phosphorus pentoxide.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + P_2O_5 \rightarrow \underset{\substack{\text{Aceto-nitrile}\\ \text{(methyl cyanide)}}}{CH_3CN} + 2HPO_3$$

$$\underset{\text{Propionamide}}{C_2H_5CONH_2} + P_2O_5 \rightarrow \underset{\substack{\text{Propiono-nitrile}\\ \text{(ethyl cyanide)}}}{C_2H_5CN} + 2HPO_3$$

Since the amides may be obtained from the corresponding acids by the dry distillation of the ammonium salt (*p.* 151), the above method of preparation of acid nitriles proves their **structural relationship** with carboxylic acids and amides :—

$$\underset{\text{Carboxylic acid}}{RCOOH} \rightarrow \underset{\text{Ammonium salt}}{R\,COONH_4} \xrightarrow{-H_2O} \underset{\text{acid amide}}{R.CONH_2} \xrightarrow{-H_2O} \underset{\text{acid nitrile}}{R.CN}$$

(2) *From Alkyl Iodides*, by heating them with an alcoholic solution of potassium cyanide, *e.g.*,

$$\underset{\text{Methyl iodide}}{CH_3I} + KCN \rightarrow \underset{\substack{\text{Methyl cyanide}\\ \text{(aceto-nitrile)}}}{CH_3CN} + KI$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KCN \rightarrow \underset{\substack{\text{Ethyl cyanide}\\ \text{(propiono-nitrile)}}}{C_2H_5CN} + KI$$

(3) *From Alkyl Potassium Sulphate*, by distilling them with dry potassium cyanide ; *e.g* ,

$$\underset{\substack{\text{Ethyl Potassium}\\ \text{sulphate}}}{C_2H_5KSO_4} + KCN \rightarrow \underset{\substack{\text{Ethyl cyanide}\\ \text{(Propiono-nitrile)}}}{C_2H_5CN} + K_2SO_5$$

Physical Properties. The lower members are colourless liquids having a strong, sweetish smell and a poisonous action. They are moderately soluble in water.

Reactions. The more important reactions of alkyl cyanides are :—

(1) *Addition of Water.* When treated with moderately concentrated sulphuric acid, the nitriles take up a molecule of water, yielding amides ; *e.g.*,

$$\underset{\text{Aceto-nitrile}}{CH_3C{\equiv}N} + H_2O \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$$

(2) *Hydrolysis.* When boiled with aqueous alkalies or dilute mineral acid, the acid nitriles get hydrolysed to give ammonia and the corres-

ponding carboxylic acids :—

$$\underset{\text{Acid nitrile}}{R.C\equiv N} \xrightarrow{+3H.OH} \underset{\text{Unstable ortho-acid}}{R.C(OH)_2.OH} + NH_3$$

$$\text{Unstable ortho-acid} \xrightarrow{-H_2O} \underset{\text{Carboxylic acid}}{R.C{<}^{O}_{OH}}$$

This reaction also proves the structural relationship between acid nitriles and carboxylic acids.

(3) *Reduction.* When reduced by means of sodium and alcohol, they are converted into **primary amines**, *e.g.*,

$$\underset{\text{Methyl cyanide}}{CH_3.C\equiv N} + 4H \rightarrow \underset{\text{Ethylamine}}{CH_3.CH_2NH_2}$$

Constitution. The constitution of alkyl cyanides follows from their formation from acid amides. Thus, in acetamide the two carbon atoms are known to be *directly* linked together and we may reasonably infer that on converting the acetamide into methyl cyanide, the two carbon atoms *remain* united :

$$\underset{\text{Acetamide}}{CH_3C{<}^{O}_{NH_2}} \xrightarrow{-H_2O} \underset{\text{Methyl cyanide}}{CH_3.C\equiv N}$$

Hence, alkyl cyanides may be assumed to possess the structural formula. R.C. ≡ N. This view is supported by their chemical behaviour (*See* reactions 1, 2, and 3 given above). All the products obtained, *viz.*, the amides, carboxylic acids. and amines have the alkyl group, originally present in the cyanide, directly linked to a carbon atom.

9. Use of Alkyl Cyanides in Organic Synthesis. Alkyl cyanides are important synthesizing agents, and are employed—

(*i*) *For the synthesis of carboxylic acids, amides and primary amines.* (*See* reactions 1, 2 and 3 given in the preceding section.)

(*ii*) **For Ascending a Series.** The formation of alkyl cyanides from alkyl halides and their reactions are utilized for ascending in series, *i. e.*, for preparing a higher member from a lower member. Thus, acetic acid may be converted into propionic acid as follows:

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{\text{Reduction}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow[\text{Reduction}]{} \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \xrightarrow{HI} \underset{\text{Ethyl iodide}}{C_2H_5I}$$

$$\xrightarrow[\text{KCN}]{\text{Alcoholic}} \underset{\text{Ethyl cyanide}}{C_2H_5CN} \xrightarrow{H.OH} \underset{\text{Propionic acid}}{C_2H_5.COOH}$$

Similarly, methyl alcohol may be converted into ethyl alcohol by the following series of reactions :—

$$CH_3OH \xrightarrow[\text{red phosphorus}]{\text{Iodine and}} CH_3I \xrightarrow[\text{KCN}]{\text{Alcoholic}} CH_3CN$$

Methyl alcohol — Methyl iodide — Methyl cyanide

$$\xrightarrow[\text{Reduction}]{} CH_3.CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH$$

Ethylamine — Ethyl alcohol

QUESTIONS

1. How would you prepare acetyl chloride ? Draw a neat sketch of the apparatus you will use, and explain, by means of equations, the action of water, ethyl alcohol, and ammonia on acetyl chloride. *(Ajmer Inter., 1930)*

2. Describe the preparation of a *pure* specimen of acetyl chloride. To what use is it put in the laboratory ? *(Punjab, Inter., 1931)*

3. How is acetyl chloride acted upon by each of the following substances : (1) water, (2) ethyl alcohol, (3) ammonia, (4) sodium acetate ? Give equations *(Cmt. Prov., Inter., 1925)*

4. Describe the preparation of acetamide. How may acetic acid, acetonitrile and methylamine be obtained from it ? *(Punjab, Inter., 1919)*

5. By what different methods can acetamide be prepared ? Describe the chemical properties of the compound. Indicate the steps necessary to convert it into methylamine. *(Cmt., Prov., Inter., 1941)*

6. An organic compound gave the following results on analysis :
(*a*) 0·197 gm. gave 0·293 gm. of carbon dioxide and 0·150 gm. of water.
(*b*) 0·118 gm. gave 22·4 c.c of Nitrogen at N. T. P.
The substance when boiled with sodium hydroxide solution evolved ammonia, and the dried residue when further heated with soda-lime gave methane.
What is the probable constitution of the original compound ?
[*Ans.* $CH_3.CO.NH_2$] *(Punjab. Inter., 1941)*

7. How do you prepare acetamide from ammonium acetate ? State the action of (*i*) nitrous acid, (*ii*) caustic soda, and (*iii*) phosphorus pentoxide, on acetamide *(Punjab, Inter., 1943)*

8. How is acetic anhydride prepared ? Give its important reactions. Why is acetic anhydride an important reagent ?

9. Write structural formulæ of the following compounds and discuss their structural relationship : (*i*) Acetic acid, (*ii*) Acetyl chloride, (*iii*) Acetic anhydride, (*iv*) Acetamide, and (*v*) Acetonitrile

10. Starting from acetic acid, how will you prepare—(*i*) formic acid (*ii*) propionic acid, $C_2H_5.COOH$, (*iii*) Methylamine, and (*iv*) Acetamide ?

11. What do you know of the preparation, properties and constitution of alkyl cyanides ? Of what use are they in organic synthesis ? *(Punjab, Inter., 1914)*

CHAPTER 15

ESTERS

1. Esterification. An ester is a compound formed by the interaction of an alcohol and an acid. Thus, when ethyl alcohol and acetic acid react together, we get an ester, called *ethyl acetate*:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Acetic acid Ethyl alcohol Ethyl acetate

The reaction between alcohol and an acid to produce an ester is called **esterification**. Esterification is a reversible reaction, since the ester produced is always hydrolysed by water to regenerate the alcohol and the acid. In order to enable the reaction to proceed as far towards the right as possible, a substance that could combine with water, and thus prevent it from hydrolysing the ester, is added to the mixture of alcohol and acid. The substances that are most suitable for this purpose are; (1) concentrated sulphuric acid, and (2) gaseous hydrogen chloride.

2. Ethyl Acetate, Acetic Ester. $CH_3COOC_2H_5$.

Preparation. (1) Ethyl acetate is prepared in the laboratory, and on the commercial scale, by the interaction of ethyl alcohol and acetic acid in the presence of concentrated sulphuric acid :—

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

The sulphuric acid serves to take up the water produced in the reaction, and thus prevents the back reaction.

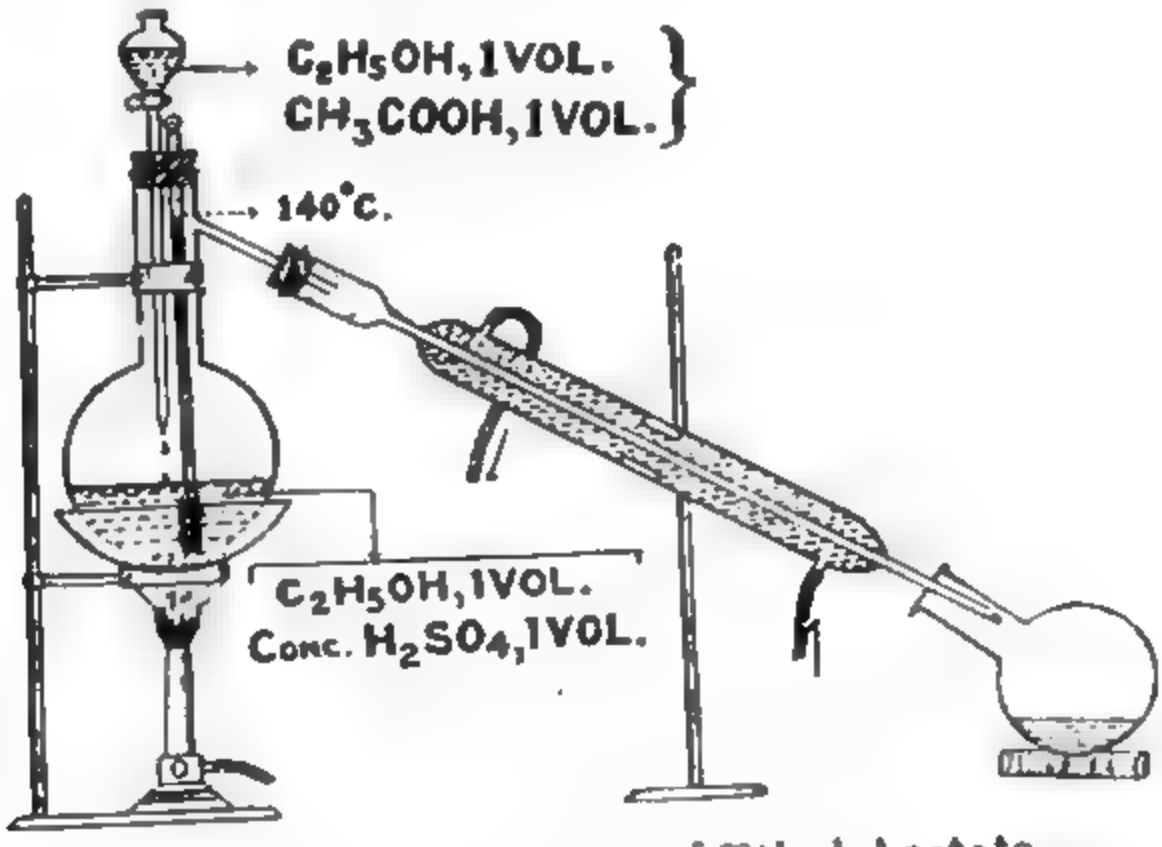


Fig. 1. Preparation of Ethyl Acetate.

Expt. 1. *Preparation of Ethyl Acetate.* A mixture of 50 c.c each of ethyl alcohol and concentrated sulphuric acid is placed in a distillation flask attached to a condenser and fitted with a dropping funnel and a thermometer, the bulb of the latter dipping completely into the liquid (Fig. 1). The flask is heated on a sand-bath until the temperature has risen to 140°C. when a mixture of 100 c.c. each of alcohol and glacial acetic acid is run in from the dropping funnel at the speed at which the liquid distils. The temperature must be kept as near 140°C. as possible throughout the experiment.

The distillate contains alcohol, acetic acid, water and sulphur dioxide, in addition to ethyl acetate. It is purified by shaking in a separating funnel; first with sodium carbonate solution, until neutral, and then with a saturated solution of common salt

to remove alcohol. The upper layer consisting of the ester, is separated and dried by allowing it to stand overnight in contact with granulated calcium chloride. It is then filtered into a dry distilling flask and distilled, the fraction boiling at 74° to 79° being collected separately.

(2) Another method for the manufacture of ethyl acetate is by the polymerization of acetaldehyde (*p.* 124).

Physical Properties and Uses. Ethyl acetate boils at 77°, and is soluble in 17 parts of water. It has a specific gravity of 0·9. On account of its refreshing perfume, it is employed in the preparation of fruit essences and in medicine. It is also used as a solvent in the manufacture of smokeless powder.

Reactions. (1) *Hydrolysis.* When ethyl acetate is heated with water under pressure, it gets hydrolysed into ethyl alcohol and acetic acid :—

$$CH_3COOC_2H_5 + H.OH \rightleftharpoons CH_3COOH + C_2H_5OH$$

A large amount of water is necessary to displace the equilibrium towards the right. The reaction is catalysed by the addition of a small quantity of a mineral acid

The hydrolysis of ethyl acetate can be carried out *quantitatively* in the presence of an alkali. The latter serves two purposes : (1) it acts catalytically and (2) it combines with the acid produced, thus making the reaction proceed to completion :—

$$CH_3COOC_2H_5 + H\,OH \rightleftharpoons CH_3COOH + C_2H_5OH$$
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$
$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH.$$

Hydrolysis of an ester by means of an alkali is termed **saponification**, as the making of soap is a useful application of this reaction.

(2) *Action of Ammonia.* When ethyl acetate is shaken with an equal volume of concentrated ammonia, it goes into solution forming acetamide and ethyl alcohol :—

$$CH_3COOC_2H_5 + NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + C_2H_5OH$$

3. Ethyl Hydrogen Sulphate, $C_2H_5.HSO_4$. This is the acid ester of sulphuric acid, and is obtained by the action of the concentrated acid on ethyl alcohol,

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O$$

The reaction is reversible, and so the yield is not quantitative.

Expt. 2. *Preparation of Ethyl hydrogen sulphate.* A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated for about one hour on a steam-bath under a reflux condenser. The reaction mixture is cooled, diluted with water, and treated with barium carbonate to neutralize the unchanged sulphuric acid and to convert ethyl hydrogen sulphate into barium ethyl sulphate. The barium sulphate and the excess of barium carbonate are filtered off, and the solution of barium ethyl sulphate is treated with cold dilute sulphuric acid, until the precipitation of barium sulphate is complete :—

$$(C_2H_5SO_4)_2Ba + H_2SO_4 \rightarrow 2C_2H_5.HSO_4 + BaSO_4$$

The solution is once again filtered, to remove brium sulphate, and then evaporated at the room temperature, under reduced pressure. Water and alcohol pass off, while ethyl hydrogen sulphate remains behind as a thick sour liquid.

Properties. Ethyl hydrogen sulphate is an odourless oily liquid. It has a strongly acidic reaction, and is miscible with water in all

proportions. The more important reactions of ethyl hydrogen sulphate are :

(1) The aqueous solution of the ester undergoes hydrolysis, yielding free sulphuric acid and ethyl alcohol, the reaction being slow at the ordinary temperature :—

$$C_2H_5.HSO_4 + H.OH \rightleftharpoons C_2H_5OH + H_2SO_4$$

(2) When heated at 160°, it yields ethylene and sulphuric acid,

$$C_2H_5.HSO_4 \rightleftharpoons C_2H_4 + H_2SO_4$$

(3) When heated with alcohol at 140°, it gives diethyl ether,

$$C_2H_5.HSO_4 + HOC_2H_5 \rightarrow \underset{\text{Diethyl ether}}{C_2H_5.O.C_2H_5} + H_2SO_4$$

(4) Being an acid ester, it neutralizes alkalies. Thus, with potassium hydroxide it gives **potassium ethyl sulphate**, which like alkyl halides, is an important synthesizing agent.

$$C_2H_5HSO_4 + KOH \rightarrow \underset{\substack{\text{potassium}\\ \text{ethyl sulphate}}}{C_2H_5KSO_4} + H_2O$$

4. Ethyl Nitrite, $C_2H_5NO_2$. This is the ethyl ester of nitrous acid, and has the structure $C_2H_5O—N=O$.

Preparation. Ethyl nitrite is prepared by the interaction of ethyl alcohol and nitrous acid. The latter, being unstable, is formed *in situ* by the action of dilute sulphuric acid on sodium nitrite.

A well-cooled mixture of equal quantities of ethyl alcohol and concentrated sulphuric acid is slowly added to a well-cooled solution of sodium nitrate in water. Brisk reaction sets in with the evolution of brown fumes of nitrogen dioxide. After the action is over the ester (which rises to the top as an oil) is separated, washed, dried over calcium chloride, and distilled.

Properties. Ethyl nitrite is a colourless, insoluble liquid with a pleasant, apple-like odour. It boils at 17°. When treated with boiling water, or dilute alkali, the ester is readily hydrolysed :

$$C_2H_5NO_2 + NaOH \rightarrow C_2H_5OH + NaNO_2$$

Distinction from Nitro-ethane. Ethyl nitrite and other alkyl nitrites differ from isomeric nitroparaffins in structure and properties (refer to Sec. 7).

Use. In the form of **sweet spirit of nitre** (which is an alcoholic solution of the ester) ethyl nitrite is used in medicine in mild febrile attacks.

5. Other Esters. Numerous other esters are known, and many of them are used as artificial perfumes and flavourings. They resemble ethyl acetate in preparation and properties.

Methyl acetate, CH_3COOCH_3 (b.p. 57°), possesses a fragrant odour, and is used as an artificial perfume.

Ethyl butyrate, $C_3H_7COOC_2H_5$, possesses an odour similar to that of pine-apple, and is used in compounding the artificial essence.

Ethyl cinnamate is used in soap perfumes and as a constituent of oriental bouquets.

Ethyl isovalerate and **ethyl malonate** both possess an apple odour, and are used in compounding the artificial fruit flavour.

Amyl acetate has the odour of pear, and is much used to impart

this flavour to confectionery.

6. Identification of an Ester. An ester can be identified by boiling it under a reflux condenser with an excess of 10 per cent sodium hydroxide solution, until no more oily drops are visible :

$$RCOO.R' + NaOH \rightarrow \underset{\text{Sodium salt of the acid}}{RCOONa} + \underset{\text{Alcohol}}{R'OH}.$$

The product is then distilled, until about one third has passed over. The distillate is examined for the alcohol, and the residual liquid in the flask for the acid component. If the alcohol be non-volatile it is extracted with ether.

The most important physical tests for an ester are the determination of its melting point and boiling-point.

7. Distinction between Esters and Salts. Esters correspond to salts of inorganic bases, but the two classes of compounds differ from each other in many respects :

(1) While neutralization of a base by an acid is an instantaneous reaction the esterification of an alcohol by an acid is a slow process. The latter is reversible, and an agent, such as sulphuric acid or gaseous hydrogen chloride must be added to "bind" the water formed and thus help the forward reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(2) Esters are usually liquids, possessing a pleasant, fruity odour, while salts are generally crystalline and possess no odour.[1]

(3) Esters are insoluble in water and are non-electrolytes. Salts, on the other hand, are electrolytes, and in aqueous solution, give the ionic reactions of the component acid and basic radicals.

(4) Salts of strong bases, *e.g.*, potassium nitrate, sodium chloride, calcium chloride, etc., are stable towards alkalies, while those of weak bases, *e.g.* cupric sulphate, ferric chloride, etc., are instantaneously decomposed by an aqueous solution of an alkali, with the precipitation of the metallic hydroxide. Esters, on the other hand, are hydrolysed by alkalies and acids only gradually, and this behaviour is common to all esters.

(5) The behaviour of salts towards aqueous ammonia is the same as with a caustic alkali. Esters, on the other hand, behave differently towards these reagents. When treated with strong, aqueous ammonia, they yield mixtures of amides and alcohols, *e.g.*,

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

8. Waxes. Waxes are mixtures of esters of higher fatty acids with higher primary alcohols. They may also contain varying proportions of these higher acids and alcohols in the uncombined state. They are insoluble in water, but dissolve in benzene, light petroleum and carbon disulphide. They may be of vegetable origin (vegetable waxes) or animal origin (**animal waxes**.) Their natural function is to protect certain tissues, against penetration by water. They find use in the manufactures, of candles, polishes, etc.

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[1] The odour of such salts as ammonium carbonate and cupric acetate is due to the basic or the acidic component, and *not* to the salt itself.

Some of the more important waxes together with their respective source, chief components and uses, are listed below :—

Wax	Source	Chief components	Characteristics and Uses
Carnauba wax.	Exuded by leaves of a palm (*Co·y-pha cerifera*) found in South America.	Melissic acid. $C_{29}H_{59}COO$	Has the property of imparting high lustre Hence used in the manufacture of polishing pastes, varnishes, etc.
Wool wax.	Natural grease contained in sheep's wool.	Esters of the unsaturated alcohol cholesterol, $C_{27}H_{45}OH$.	Has the valuable property of yielding emulsions with water which are easily absorbed by skin. Hence used as a basis for ointments and cosmetics
Beeswax.	Secreted by the common bee (*Apis mellifica*) as a product of digestion.	Mixture of cerotic acid, $C_{25}H_{51}COOH$. and myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$.	Boot polishes, cosmetics, lithographic ink.
Spermaceti.	Occurs in head cavities and blubber of sperm whale.	Cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$.	Brittle and powderable. Used in making sperm candles, cerates and cosmetics.
Chinese wax.	Is the secretion of an insect (*Coccus ceriferus*) larvæ of which infest the bark and twigs of the evergreen tree *Ligustrum lucidum* found in Western China.	..	Used for making candles, polishing furniture and leather, etc.

QUESTIONS

1. What are esters ? How do they differ from salts ? *(Unit. Prov., Inter., 1922)*

2. (*a*) What are the typical properties of an ester ? Illustrate your answer with reference to ethyl acetate.

(*b*) Are the following compounds *esters* or *salts* ? :—Ethyl sulphate, ethyl oxalate, ammonium acetate, methylamine formate, sodium bicarbonate. *(Unit. Prov., Inter., 1925)*

3. Describe fully the preparation of a sample of pure ethyl acetate in the laboratory and give its properties. Give equations where necessary.

4 Describe the preparation of a pure sample of ethyl acetate in the laboratory. Give the important properties of this compound

5. Ethyl formate and methyl acetate possess the same molecular formula viz., $C_3H_6O_2$. If you were given both these compounds, how will you proceed to find which is which ?

6. What are the methods commonly used for the esterification of an acid? Illustrate with reference to acetic acid. How are the components of an ester identified ? *(Ajmer, Inter., 1932)*

7 A pleasant-smelling organic liquid was found to contain C=18·6 per cent and H=8·1 per cent. When boiled with an aqueous solution of caustic soda, it gave methyl alcohol. The alkaline residue when evaporated to dryness and heated with dry soda lime gave off a gas, which proved to be methane. What was the original liquid ? explain the above reactions

(Ans. Methyl acetate, CH_3COOCH_3)

8 How would you distinguish an acid from an ester, both of which had the same molecular formula $C_4H_8O_2$? How would you proceed to determine the nature of the acid and alcohol combined in an ester of the above formula ?

(Unit. Prov., Inter , 1924)

9. Write full structural formulae of the following esters :— (i) Ethyl acetate, (ii) Methyl acetate ; (iii) Ethyl formate. How may each of these compounds be regarded as derived from methane.

CHAPTER 16

FATS, OILS AND SOAPS

1. Fats and Oils. Fats and oils are mixtures of normal glyceryl esters of higher fatty acids, notably those of palmitic acid, $C_{15}H_{31}.COOH$ and stearic acid, $C_{17}H_{35}.COOH$, and certain unsaturated acids; such as oleic acid, $C_{17}H_{33}C.OOH$. The name of a glycerol ester is derived from the acid that it contains and it has the suffix *-in* attached to it. Thus palmitin or glyceryl tripalmitate, which is the chief constituent of palm oil, is formed by the combination of three molecules of the monobasic palmitic acid with one molecule of the trihydric alcohol, glycerol:—

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \\ \text{Glycerol} \end{array} + 3\underset{\text{Palmitic acid}}{C_{15}H_{31}.COOH} \rightarrow \begin{array}{l} C_{15}H_{31}COO.CH_2 \\ | \\ C_{15}H_{31}COO.CH \\ | \\ C_{15}H_{31}COO.CH_2 \\ \text{Palmitin} \end{array} + 3H_2O.$$

Similarly, stearin and olein possess the formulae,

$$\begin{array}{l} C_{17}H_{35}COO.CH_2 \\ | \\ C_{17}H_{35}COO.CH \\ | \\ C_{17}H_{35}COO.CH_2 \\ \text{Stearin} \end{array} \quad \text{and} \quad \begin{array}{l} C_{17}H_{33}COO.CH_2 \\ | \\ C_{17}H_{35}COO.CH \\ | \\ C_{17}H_{33}COO.CH_2 \\ \text{Olein} \end{array}$$

2. Properties of Fats and Oils. While the two fatty acids, palmitic, and stearic are solids (melting respectively at 62° and 69°), the unsaturated oleic acid is a liquid. Corresponding to this the glyceryl esters derived from the fatty acids are solids, while that derived from oleic acid is a liquid. The consistency of a particular fat or oil depends, of course, on the relative proportions of the three esters that it contains. Thus palm oil of which the chief constituent is palmitin, has the consistency of butter, while olive oil, which contains about 75 per cent of olein is a liquid. The animal fat contains 75 per cent of stearin and palmitin and 25 per cent of olein. It has a solid consistency in the cold weather; at the body temperature, it is a liquid. *Ghee* (butter fat) differs from all other fats and oils (except cocoa-nut) in containing a large proportion (7·7 per cent) of butyrin.

Fats or oils are insoluble in water and sparingly soluble in alcohol. They are readily soluble in petrol, benzene, kerosene oil, chloroform and ether. They are specifically lighter than water. They are non-volatile, and when heated strongly they undergo decomposition.

Certain oils, *e.g.*, *linseed oil* when exposed to air, undergo hardening, owing to the absorption of atmospheric oxygen. The process is known as *drying* and an oil possessing the property of drying is called a **drying oil**. Other examples of drying oils are *tung oil*, *hemp seed oil* and *poppy oil*. Drying oils are extensively used in making paints. Olive oil is a **non-drying oil**, as it lacks the property of dying. Cotton seed oil, castor oil, etc., possess the property of drying, though to a smaller extent than the typical drying oils referred to above. They are, therefore, **semidrying oils**.

The two important reactions of fats and oils are: (1) hydrogenation and (2) saponification.

3. Hydrogenation of Oils. This process consists in the direct addition of hydrogen to oils in the presence of finely divided nickel, whereby the liquid glyceride *olein* is partially converted into the solid glyceride *stearin* :

$$\begin{array}{l} C_{17}H_{33}COO.CH_2 \\ | \\ C_{17}H_{33}COO.CH \\ | \\ C_{17}H_{33}COO.CH_2 \\ \text{Olein (liquid)} \end{array} + 3H_2 \xrightarrow{Ni} \begin{array}{l} C_{17}H_{35}COO.CH_2 \\ | \\ C_{17}H_{35}COO\ CH \\ | \\ C_{17}H_{35}COO.CH_2 \\ \text{Stearin (solid)} \end{array}$$

This reaction is analogous to the conversion of ethylene into ethane and forms the basis of the manufacture of **artificial ghee** from vegetable oils.

4. Saponification of Fats and Oils: Soap. Fats and oils, like other esters, are hydrolysed by solutions of caustic alkalies. The products of hydrolysis in this case are (1) glycerol, and (2) **soap,** *i.e.*, a mixture of sodium salts of the acids present. In the case of *stearin*, which is a typical constituent of fats and oils, the change may be represented by the equation:

$$\begin{array}{l} C_{17}H_{35}COO\ CH_2 \\ | \\ C_{17}H_{35}COO.CH \\ | \\ C_{17}H_{35}COO.CH_2 \\ \text{Stearin} \\ \text{(Glyceryl tristearate)} \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3\underset{\substack{\text{Sodium stearate} \\ \text{(a soap)}}}{C_{17}H_{35}COONa}$$

Palmitin and *olein*, the other two constituent of fats and oils, are similarly decomposed to give glycerol and sodium salts of palmitic and oleic acids

Since the hydrolysis of a fat or oil by means of caustic alkali results in the formation of soap, the reaction is called **saponification.** The saponification of fats and oils is carried out on a large scale by the following two processes :—

(1) **Cold Process.** This process consists in the saponification of fats and oils by means of a concentrated solution of sodium hydroxide, the glycerol produced being left in the soap.

A weighed amount of the fat or oil is placed in an iron vessel, provided with a stirring arrangement, and is brought to the proper temperature (65°C in cold weather and 50°C in hot). A calculated quantity (usually 75 per cent by weight of the fat or oil used) of a concentrated solution (sp. gr 1·3·5) of commercial caustic soda (74%) is then rapidly run in, and the mixture thoroughly stirred, until it has assumed the consistency of a thick paste. This is run out into a soap frame, which consists of a large size wooden or iron box with detachable sides, and mounted wheels. The frame is well covered up to keep in the heat. The reaction between fat and alkali proceeds with considerable heat evolution, and is over in two days time in the case of a small batch. Usually, however, a week or so is allowed to elapse before the soap is taken out of the frame.

(2) **Hot Process.** This process is at present employed on the largest scale. It is carried out in a *soap kettle,* which consists of a large cylindrical vessel fitted with an open steam coil for heating the contents. A measured quantity of fat or oil is run into the soap kettle, and then a dilute solution of caustic soda (sp. gr. 1·117) amounting to about one-quarter of the theoretical quantity is introduced. Steam is turned on, and the mixture vigorously boiled An emulsion is first formed and as the alkali is taken up by the fat, additional amounts are gradually run in, till finally an *excess* is present, and the mass has become clear and homogeneous.

Dry sodium chloride is now shovelled into the mass to throw the soap out of solution, the mixture well boiled, and then allowed to settle. It separates out into a layer of soap above and 'spent lye' (*i. e.*, aqueous solution containing glycerol, excess of NaOH, and NaCl) below. The lower layer of spent lye is run off. During the above process, water is withdrawn from the soap to dissolve the dry salt ; hence the soap loses its transparency, and assumes a 'grain-like' appearance. The process is, therefore, termed 'graining' the **soap.**

The curdy mass of soap is now boiled up with water, to form a homogeneous mass, a fresh quantity of caustic soda solution is added, and the boiling continued to ensure complete saponification of the fat. Finally, the lye is again separated by the addition of salt. The process is sometimes repeated to eliminate, along with the lye, impurities which spoil the colour of soap

Finally, the open soap is boiled up with water, until a homogeneous mass is obtained It is then allowed to settle for a few days, when there is found at the bottom of the pan a small amount of dark-coloured lye ; above this there is a layer of dark-coloured soap (which owes its colour to the presence of iron soap and other impurities). On the top of the latter lies the large bulk of "neat soap"

The upper layer of neat soap, whilst still warm, is run into soap frames, where it solidifies and hardens. The frames are then opened up, and the soap cut first into slabs and then into bars.

Expt. 1. *Preparation of Soap.* Place 25 grams of cocoa-nut oil in a porcelain dish. And a solution of 5 grams of caustic soda in 80 c.c of water. Boil gently with continuous stirring. In about half an hour the oil disappears completely. Now add about 80 c.c. of a saturated solution of common salt. Stir well, and set aside to cool. The soap will separate as a cake on the surface. Remove it with a spatula. Wash the soap with dilute sodium chloride solution. Draw off the liquid and set the soap aside to dry in the air.

5. Soaps Soaps are mixtures of sodium or potassium salts of the acids present in fats and oils As already described, they are prepared by two different processes, the *cold* process and the *hot* process. They are divided into two chief classes, *viz.*, **hard soaps** and **soft soaps.** In the former, which are far more common, caustic soda is employed for effecting saponification of the fat or oil, while in the latter caustic potash is used for this purpose. Soft soaps are put on the market in the form of a paste.

Soaps are colloidal in nature. When dissolved in water, they give colloidal solutions, which can readily bring the greasy matter into the form of a colloidal solution. On this fact is based the **cleaning action** of soap. With the removal of grease, the dirt particles are detached from the surface of the cloth, and are washed away.

6. Uses of Fats and Oils. Fats and oils find numerous applications, the more Important of which are :—

(1) As food for man and animals.

(2) For the manufacture of soap, glycerol and stearine candles.

(3) In making paints.

(4) *In Pharmacy.* Thus, cold-pressed castor oil and croton oil are used as purgatives Almond oil is used both internally and externally. Cod-liver oil is prescribed in wasting diseases.

(5) *As Lubricants.* Lower grades of castor oil, certain fish oils, *sarson* oil, and many others are used as lubricants.

(6) *As Hair Oils.* Refined vegetable oils of non-drying character are used as hair oils.

(7) *As Illuminants.* Sarson oil is much used as an illuminant in villages of the Punjab. Other vegetable oils and flish oils are used similarly.

(8) oils are also used in making oil-cloth, linoleum, printing inks, and insulating materials, in leather and wool dressing and in the tempering of steel, etc.

7. Mineral Oils. Mineral oils derived from petroleum. They are mixtures of liquid *hydrocarbons* of the paraffin and other series. Hence, though resembling in physical properties with vegetable and animal oils (which, as mentioned above, are esters), they differ from them entirely in their chemical behaviour. Thus, while vegetable and animal oils are hydrolysed by alkalies to produce soap, mineral oils are stable towards alkalies, and cannot, therefore, be employed in soap manufacture.

Kerosene oil, petrol, lubricating oils, and liquid paraffin are examples of mineral oils.

QUESTIONS

1. What is the nature of fats and oils derived from the bodies of animals and plant seeds ? In what respects do they differ from mineral oils ? Give three different examples of (*a*) vegetable oils, and (*b*) mineral oils.

2. Compare the properties of fats and soaps, and hence show how you could distinguish them experimentally. (*Unit. Prov., Inter., 1928*)

3. What is soap ? Can soap be prepared from kerosene oil ? Describe briefly the manufacture of soap. (*Unit. Prov., Inter., 1921*)

4. What do you understand by the term *Saponification* ? Give examples of this process in the laboratory as well as in the factory. (*Punjab. Inter., 1930*)

5. Write notes on —(*a*) drying oils, (*b*) hydrogenation of oils , (*c*) hard and soft soaps, and (*d*) cleansing action of soap.

6. What is the action of a boiling solution of caustic soda on the following substances:— (*a*) Acetaldehyde, (*b*) Acetamide, (*c*) Chloroform, (*d*) Fats ? (*Unit. Prov., Inter., 1930*)

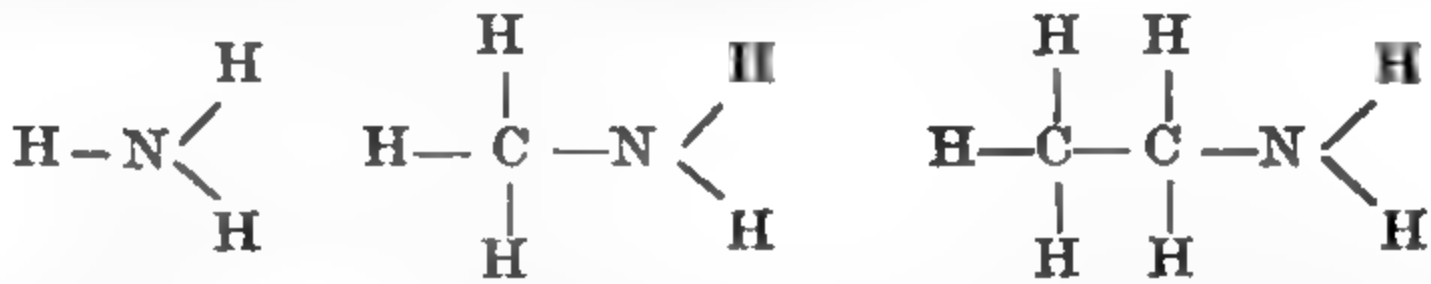
7. State in detail the method you would use in preparing a sample of soap free from oil and excess of alkali. (*Unit. Prov., Inter., 1930*)

8. What are oils and fats, and how do they differ from mineral oils ? What are their uses ? Describe the processes for the manufacture of soap, and explain its cleansing action. (*Punjab. Inter., 1944*)

CHAPTER 17

AMINES AND NITROPARAFFINS

1. Amines. The amines are derived from ammonia, NH_3, by the replacement of hydrogen by alkyl groups. The structural formulae of ammonia, methylamine, and ethylamine, given below will show the structural relationship of these compounds :—



Ammonia — Methylamine — Ethylamine

It is evident that methylamine is derived from ammonia by the replacement of a hydrogen atom of the latter by a methyl group. Similarly, ethylamine is derived from ammonia by the replacement of a hydrogen atom by an ethyl group.

Methylamine and ethylamine are examples of primary amines, and contain the amino-group, — NH_2, in their molecules. When two or three atoms of hydrogen in ammonia are replaced by alkyl groups, we get **secondary amines** and **tertiary amines** respectively. The simplest examples of secondary and tertiary amines are :—

$(CH_3)_2.NH$ and $(CH_3)_3N$

Dimethylamine (a *secondary* amine) — Trimethylamine (a *tertiary* amine)

The alkyl groups in a secondary or a tertiary amine may be all identical, as in dimethylamine and trimethylamine, or they may be different, as in methylethylamine, $\begin{matrix}CH_3\\C_2H_5\end{matrix}>NH$, or dimethylethylamine, $\begin{matrix}CH_3\\CH_3\end{matrix}>N.C_2H_5$. In the former case, the amine is said to be a **simple amine** and in the latter, a **mixed amine** (compare ethers).

2. Primary Amines, $R.NH_2$. We shall discuss Methylamine, $CH_3.NH_2$, and Ethylamine, $C_2H_5.NH_2$, as typical examples of primary amines. Other amines of this class may be prepared by methods analogous to those described in these cases, and possess exactly identical properties. The chemical properties in which primary amines *differ* from secondary and tertiary amines are discussed in Sec. 161.

3. Methylamine, $CH_3.NH_2$.

Preparation. Methylamine may be prepared by the following methods :—

(1) *From Methyl Iodide* (**Hofmann's alkylation method**). When methyl iodide is heated with an alcoholic or aqueous solution of ammonia in a sealed tube, we get, among other products[1], methylamine hydriodide[2] :—

$$CH_3I + HNH_2 \rightarrow \underset{\text{Methylamine}}{CH_3NH_2} + HI \rightarrow \underset{\text{Methylamine hydriodide}}{CH_3NH_2.HI}$$

[1] See under *Secondary and Tertiary Amines* (Sec. 160).

[2] More correctly *methylammonium iodide*, $(CH_3NH_3)I$.

The reaction clearly shows the structural relationship of methyliodide and methylamine.

AUGUST WILLIAM HOFMANN (1818—1892)
distinguished pupil of Liebig. He is well known for his work on amines and the organic bases present in coal tar.

(2) *From Methyl Alcohol.* When a mixture of methyl alchohol vapour and ammonia is passed over heated alumina or thoria, methylamine (together with di- and trimethylamines) is produced :

$$CH_3OH + HNH_2 \rightarrow \underset{\text{Methylamine}}{CH_3NH_2} + H_2O$$

(3) *From Hydrogen Cyanide.* Methylamine is also produced when hydrogen cyanide is reduced by means of metallic sodium and alcohol :-

$$\underset{\text{Hydogen cyanide}}{HCN} + 4H \rightarrow \underset{\text{Methylamine}}{CH_3.NH_2}$$

(4) *From Acetamide* (**Hofmann's bromamide reaction**) See *p.* 152.

Properties. (1) Methylamine is a colourless gas possessing an ammoniacal odour, and like ammonia is exceedingly soluble in water. It burns in air with a yellow flame.

(2) *Basic Nature.* Methylamine, like ammonia, is a basic anhydride. Its aqueous solution contains methylammonium hodroxide.

$$CH_3NH_2 + H.OH \rightleftharpoons \underset{\substack{\text{Methylammonium}\\\text{hydroxide}}}{(CH_3NH_3)OH}$$

which is a stronger base than ammonia, and ionizes to give hydroxidion

and methylammonium ion :—

$$(CH_3NH_3)OH \rightleftharpoons (CH_3NH_3)^+ + OH^-$$

For this reason, an aqueous solution of methylamine turns red litmus blue and turmeric brown. It neutralizes acids and precipitates the hydroxides of heavy metals from aqueous solutions of their salts ; *e. g.*

$$\underset{\text{Methylammonium hydroxide}}{CH_3NH_3OH} + HI \rightarrow \underset{\text{Methylammonium iodide}}{CH_3NH_3I} + H_2O$$

$$FeCl_3 + 3CH_3NH_3OH \rightarrow \underset{\text{Ferric hydroxide}}{Fe(OH)_3} + 3CH_3NH_3Cl$$

Like ammonium chloride, methylammonium chloride combines with platinic chloride to give a yellow, crystalline platini chloride having the formula $(CH_3NH_3)_2[PtCl_6)$.

(3) *Action of Nitrous Acid.* When treated with nitrous acid, methylamine yields methyl alcohol, nitrogen and water (compare the action of this reagent on ammonia and also on acetamide, *p.* 152) :—

$$\begin{matrix} CH_3NH_2 \\ +HONO \end{matrix} \rightarrow \underset{\text{Methyl alcohol}}{CH_3.OH} + N_2 + H_2O$$

(4) *Alkylation.* Methylamine and other primary amines, resemble ammonia in reacting with alkyl halides, yielding secondary and tertiary amines and quaternary ammonium salts (Sec. 163).

(5) *Acylation.* It further resembles ammonia in reacting with acid chlorides, yielding substituted amides ; *e.g.*

$$\underset{\text{Acetyl chloride}}{CH_3CO{:}Cl} + H{:}NH(CH_3) \rightarrow \underset{\text{N-methyl acetamide}^1}{CH_3.CO.NH(CH_3)} + HCl.$$

(6) **Carbylamine Reaction.** When methylamine is warmed with two or three drops of chloroform and a little alcoholic potash, a highly disgusting odour of methyl carbylamine is produced :—

$$CH_3NH_2 + CHCl_3 + 3KOH \rightarrow \underset{\substack{\text{Methyl} \\ \text{carbylamine}}}{CH_3NC} + 3KCl + 3H_2O$$

The reaction is used for the identification of primary amines and of chloroform (compare *p.* 87).

4. Ethylamine, $C_2H_5.NH_2$. Ethylamine closely resembles methylamine. It may be prepared from (1) ethyl iodide, (2) ethyl alcohol, (3) methyl cyanide and (4) propionamide by methods analogous to those described above for methylamine.

(1) $\underset{\text{Ethyl iodide}}{C_2H_5I} + NH_3 \rightarrow \underset{\text{Ethylamine hydriodide}}{C_2H_5NH_2\,HI}$

(2) $\underset{\text{Ethyl alcohol}}{C_2H_5OH} + NH_3 \rightarrow \underset{\text{Ethylamine}}{C_2H_5.NH_2} + H_2O$

(3) $\underset{\text{Methyl cyanide}}{CH_3CN} + 4H \rightarrow \underset{\text{Ethylamide}}{CH_3.CH_2.NH_2}$

(4) (*i*) $\underset{\text{Propionamide}}{C_2H_5.CO.NH_2} \xrightarrow{Br + KOH} \underset{\text{Propionbromamide}}{C_2H_5.CO.NHBr}$

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1. The letter N here indicates that the methyl group has replaced one of the hydrogens linked to the *nitrogen* atom of the acetamide molecule.

(*ii*) $C_2H_5CO\,N\,HBr \xrightarrow{KOH} C_2H_5.NH_2 + CO_2 + HBr$
$\quad + \quad O\,H_2$ — Ethylamine

Properties. (1) Ethylamine is a colourless gas above 19°. At this temperature, it liquefies to give a colourless liquid. Ethylamine closely resembles methylamine in properties. It has an ammoniacal odour, is highly soluble in water, and burns with a yellow flame.

(2) Ethylamine, like methylamine, possesses basic properties. Its aqueous solution contains ethylammonium hydroxide, $C_2H_5NH_3OH$. It turns red litmus blue, neutralizes acids and precipitates the hydroxides of heavy metals from solution of their salts. It also forms a yellow platinichloride of the formula $(C_2H_5NH_3)_2[PtCl_6]$

(3) It reacts with nitrous acid to give ethyl alcohol, nitrogen and water :—

$$\begin{matrix} C_2H_5\,N\,H_2 \\ +HO\,N.O \end{matrix} \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2 + H_2O$$

(4) It reacts with *alkyl halides*, yielding secondary and tertiary amines and quaternary ammonium salts (Sec. 160).

(5) It also reacts with *acid chlorides*, yielding substituted amides, *e. g.*,

$$\underset{\text{Acetyl chloride}}{CH_3CO\,Cl} + H\,NH(C_2H_5) \rightarrow \underset{\text{N-ethyl acetamide}}{CH_3.CO.NH(C_2H_5)} + HCl$$

(6) When warmed with chloroform and alcoholic potash it yields ethyl carbylamine, which possesses a highly disgusting odour :—

$$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow \underset{\text{Ethyl carbylamine}}{C_2H_5NC} + 3KCl + 3H_2O$$

The reaction may be used as a test for ethylamine.

5. Secondary and Tertiary Amines. In **Hofmann's method** for the alkylation of ammonia (*p.* 208) we get a *mixture* of four different products, *viz* , the salts of primary, secondray and tertiary amines and quaternary ammonium salt (See. 162). Thus, with ethyl iodide the reaction proceeds in the following stages, which proceed *simultaneously*.

(*i*) $C_2H_5\,I + H.NH_3 \rightarrow \underset{\text{Ethylamine hydriodide}}{C_2H_5NH_2.HI}$

(*ii*) $C_2H_5\,I + H\,NH(C_2H_5) \rightarrow \underset{\text{Diethylamine hydriodide}}{(C_2H_5)_2NH,HI}$

(*iii*) $C_2H_5\,I + H\,N(C_2H_5)_2 \rightarrow \underset{\text{Triethylamine hydriodide}}{(C_2H_5)_2N,HI}$

(*iv*) $C_2H_5I + N(C_2H_5)_3 \rightarrow \underset{\text{Tetraethylammonium iodide.}}{[(C_2H_5)_4N]I}$

Separation. The mixture of the above salts is distilled with *potassium hydroxide*, when the primary, secondary and tertiary amines pass over. The quaternary ammonium salt, being not decomposed by alkali, is left behind.

From the distillate, the three amines can be separated by various methods.

The three amines present in the distillate may be separated from each other by *fractional distillation*. This is possible only in the case of propylamines and the higher members. The lower amines *viz* , methylamines and ethylamines *cannot* be separated by fractional distillation,

since in these cases the boiling points of primary, secondary and tertiary amines are far too near. They can, however, be separated by *fractional crystallization* of the hydrochlorides.

A general method (**Hinsberg's method**) for the separation of the three amines is as follows :—

(*i*) The mixture is treated with *benzene sulphonic chloride*,[1] $C_6H_5SO_2Cl$, when the primary and secondary amines react, yielding mono- and di-alkyl substituted amides :

$$C_6H_5SO_2Cl + \underset{\text{Primary amine}}{NH_2R} \rightarrow \underset{\text{Monalkyl benzene sulphonic amide}}{C_6H_5SO_2NHR} + HCl$$

$$C_6H_5SO_2Cl + \underset{\text{Secondary amine}}{NHR_2} \rightarrow \underset{\text{Dialkyl benzene sulphonic amide}}{C_6H_5SO_2NR_2} + HCl$$

The teriary omines, since they contain no hydrogen linked to nitrogen, do not react.

(*ii*) The reaction mixture is strongly alkalified with *potassium hydroxide*, when the primary-amine derivative dissolves forming the potassium salt, $C_6H_5SO_2NKR$. The secondary-amine derivative, since it contains no hydrogen linked to nitrogen, remains undissolved.

(*iii*) The alkaline liquid is now *extracted with ether*, when the tertiary amine and the secondary-amine derivative pass into the ethereal layer. The potassium salt of the primary-amine derivative is left behind in the aqueous layer.

(*iv*) The *aqueous layer* is strongly acidified, when monalkyl benzene sulphonic amide is precipited.

$$C_6H_5SO_2NKR + HCl \rightarrow C_6H_5SO_2NHR + KCl,$$

which, after being separated, is hydrolysed by boiling with concentrated hydrochloric acid :—

$$C_6H_5SO_2NHR + H.OH + HCl \rightarrow C_6H_5.SO_2OH + RNH_2.CHl$$

The resulting solution, containing the hydrochloride of the primary amine, is distilled with sodium hydroxide to recover the primary amine:—

$$RNH_2\,HCl + NaOH \rightarrow RNH_2 + NaCl + H_2O$$

(*v*) The *ethereal layer* is subjected to fractional distillation, in order to separate the tertiary amine and the derivative of the secondary amine. The latter is then hydrolyed by boiling with concentrated hydrochloric acid,

$$C_6H_5SO_2NR_2 + H.OH + HCl \rightarrow C_6H_5SO_2OH + R_2NH.HCl,$$

and the product distilled with sodium hydroxide to recover the secondary amine:

$$R_2NH.HCl + NaOH \rightarrow R_2NH + NaCl + H_2O$$

Properties. The secondary and tertiary amines resemble primary amines in being colourless gases or volatile liquids having a strongly ammoniacal and fishy odour. They are stronger bases than primary amines, and dissolve in water to give strongly alkaline solution they form salts with acids, precipitate the heavy metal hydroxides from aqueous solutions of their salts, and form crystalline platinichlorides.

[1] This reacts like other acid chlorides (compare *p.* 211).

The three classes of amines differ from each other in certain important points which are discussed below.

6. Distinction between Primary, Secondary and Tertiary Amines :—

(1) *Action of Nitrous Acid.* While the primary amines, as already stated (*p.* 209) react with nitrous acid, yielding primary alcohols and nitrogen, the secondary amines give yellowish-red oily liquids called nitrosamines :

$$R_2N\ddot{H} + \ddot{H}O\,NO \rightarrow R_2N.NO + H_2O$$

Secondary amine — Nitrous acid — nitrosamine

Nitrosamines can be readily identified by warming them with phenol and concentrated sulphuric acid pouring the product into water, and alkalifying, when a deep blue or violet coloration is developed (**Liebermann's nitroso reaction**). This affords a characteristic test for the **identification of secondary amines.**

Expt. 1. To a concentrated solution of diethylamine in hydrochloric acid add a concentrated solution of sodium nitrite. Extract the resulting nitrosamine with ether, and wash the ethereal layer with water to completely free it from nitrous acid. Evaporate off the ether, and apply Libermann's reaction.

Tertiary amines do not react with nitrous acid.

(2) *Action of Acid Chlorides.* As already stated (*p.* 211), primary amines react with acid chlorides, yielding monoalkyl derivatives of amides. Secondary amines react similarly, yielding dialkyl derivatives of amides ; *e.g.*,

$$CH_3CO\,\underline{\ddot{Cl} + H}\,N(CH_3)_2 \rightarrow CH_3CON(CH_3)_2$$

Acetyl chloride — Dimethylamine — Dimethylacetamide

Tertiary amines, since they contain no hydrogen atom linked directly to nitrogen, do *not* react with acid chlorides.

Benzene sulphonic chloride; $C_6H_5SO_2Cl$, as already stated (*p.* 212), has been emloyed by Hinsberg for the separation of the three clases of amines from one another.

(3) *Carbylamine Reaction.* This is given only by primary amines (*p.* 210), and may, therefore, be utilized for distinguishing primary amines from the secondary and tertiary amines

7. Ascent and Descent of Homologous Series. Formation of a primary amine may be employed for the ascent or descent of a homologous series In the former case, the additional carbon atom is introduced in the form of a—CN group, which may be reduced to the—CH_2NH_2 group by Mendius reaction, The resulting amine may then be converted into an alcohol by treatment with nitrous acid as in Example 1, given below.

The descent of a homologous series is effected through Hofmann's bromamide reaction as in Examples 2 and 3, given below.

Examples :—

(1) *Conversion of Methyl Alcohol into Ethyl Alcohol :—*

$$CH_3OH \xrightarrow{P+I} CH_3I \xrightarrow{KCN} CH_3CN$$

Methyl alcohol — Methyl iodide — Methyl cyanide

$$\xrightarrow{\text{Rduction}} \underset{\text{Ethylamine}}{CN_3.CH_2.NH_2} \xrightarrow{\text{Nitrous acid}} \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

(2) *Conversion of Ethyl Alcohol into Methyl Alcohol :—*

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{\text{Oxidation}} \underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\xrightarrow{\text{Heat the ammonium salt}} \underset{\text{Acetmide}}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

$$\xrightarrow{\text{Nitrous acid}} \underset{\text{Methyl alcohol}}{CH_3OH}$$

(3) *Conversion of Acetic into Formic Acid :—*

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{\text{Heat the ammonium salt}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

$$\xrightarrow{\text{Nitrous acid}} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{\text{Oxidation}} \underset{\text{Formic acid}}{H.COOH}$$

8. Quaternary Ammonium Compounds. Tertiary amines combine with alkyl iodides to form a class of compounds called quaternary ammonium salts ; *e.g.*,

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3I \rightarrow \underset{\substack{\text{Letramethylammonium iodide}\\ \text{(a quaternary ammonium salt)}}}{[(CH_3)_4N]I}$$

These salts, on treatment with silver hydroxide, give quaternary ammonium hydroxides, *e.g.*,

$$(CH_3)_4NI + AgOH \rightarrow \underset{\substack{\text{Tetramethyl ammonium}\\ \text{hydroxide}}}{[(CH_3)_4N]OH} + AgI$$

The latter compounds are very strong bases (nearly as strong as KOH). They are exceedingly soluble in water, and the solutions show a strongly alkaline reaction, owing to ionization :

$$(CH_3)_4NOH \rightleftharpoons (CH_3)_4N^+ + OH^-$$

The structure of quaternary ammonium salts is similar to that of ammonium salts. They are electrovalent compounds, and, as already stated, ionize to a very considerable extent In the tetralkylammonium-ion, the nitrogen atom is *tetracovalent*, as shown below in the case of tetramethylammonium iodide :—

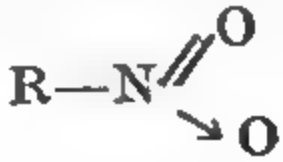
$$\left\{ \begin{array}{c} CH_3 \\ | \\ CH_3—N—CH_3 \\ | \\ CH_3 \end{array} \right\}^+ I^-$$

9. Nitro-Paraffins Nitro-paraffins are derived from paraffin hydrocarbons by the replacement of a hydrogen atom by a nitro-group, $—NO_2$. Thus, methane, CH_4, and ethane, C_2H_6, give rise to nitro-methane and nitro-ethane respectively :

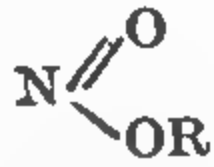
CH_3NO_2
Nitro-methane
(b.p. 101°)

$C_2H_5NO_2$
Nitro-ethane
(b.p. 115°)

Nitro-paraffins are isomeric with alkyl nitrites, *i.e.* the esters, of nitrous acid. The two classes of compounds are given the following structural formulæ. :—



Nitro-paraffins



Alkyl nitrites

The nitrogen atom in nitro-paraffins is tetracovalent; in alkyl nitrites it is tricovalent. One of the oxygen atoms in the nitro-group is linked to the nitrogen atom by an ordinary double bond and the other by a co-ordinate link (see page 55).

Nitro-paraffins are divided into three classes, corresponding to three classes of alcohols (*p.* 112) :—

Primary Nitro-paraffins, $RCH_2.NO_2$
Secondary Nitro-paraffins, $R_2CH.NO_2$
Tertiary Nitro-paraffins, $R_3C.NO_2$

Preparation. Nitro-paraffins are prepared by distilling alkyl iodides with silver nitrite :—

$$\underset{\text{Methyl iodide}}{CH_3I} + AgNO_2 \rightarrow \underset{\text{Nitro-methane}}{CH_3.NO_2} + AgI$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + AgNO_2 \rightarrow \underset{\text{Nitro-ethane}}{C_2H_5.NO_2} + AgI$$

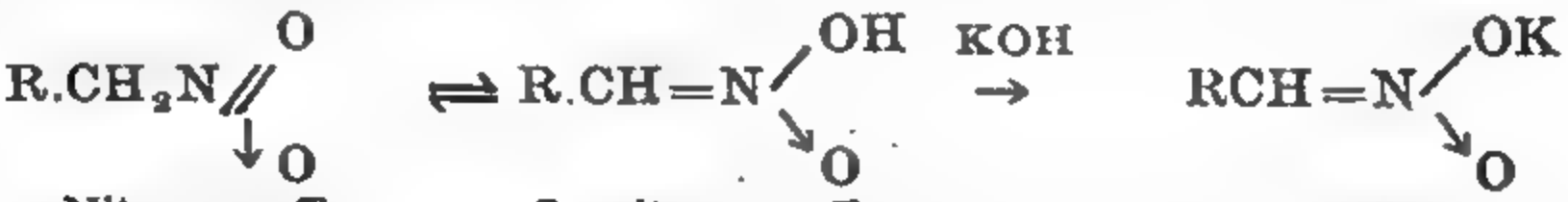
Some alkyl nitrites are also produced in this reaction but can be readily separated by fractional distillation[1].

Physical Properties. Nitro-paraffins are colourless liquids having a pleasant odour. They boil at much higher temperature than the isomeric nitrites (*see* foot note). The lower members are lightly soluble in water : the higher ones are practically insoluble,

Reactions. (1) *Reductions.* When submitted to reduction (tin and hydrochloric acid), nitro-paraffins yield primary amines ; *e.g.*

$$\underset{\text{Nitro methane}}{CH_3NO_2} + 6H \rightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O$$

(2) *Action of alkalies.* Primary and secondary nitroparaffins (but *not* the tertiary) *gradually* dissolve in alkalies, yielding salts derived from isonitro-paraffins; *i.e., the salt formation is preceded by a change of constitution* :—



Nitro-paraffin — Isonitro-paraffin — Potassium salt

A substance, such as a nitro-paraffin, which though itself not an acid, can, by a change of constitution, pass into another that can function as a true acid is termed a pseudo-acid.

(3) *Action of Nitrous Acid.* Primary, secondary and tertiary

[1]The nitro-paraffins boil at much higher tempratures than the alkyl nitrites. Thus while ethyl nitrite boils at 16°, nitro-ethane boils at 115°.

nitro-paraffins behave differently towards nitrous acid. This fact forms the basis of **Victor Meyer's method** for distinguishing the three classes of alcohols from one another. (Refer to *p.* 116)

10. Distinction between Nitro-paraffins and alkyl Nitrates :—

(1) *Boiling Points.* As already mentioned, nitro-paraffins boil at much higher temperatures than alkyl nirites

(2) *Reduction.* Upon reduction with tin and hydrochloric acid nitroparaffins yield the corresponding primary amines (*see* above) whilst alkyl nitrites, under the same conditions, undergo hydrolysis, followed by reduction of the resulting nitrous acid to ammonia or hydroxylamine : *e.g.*,

$$C_2H_5NO_2 + H.OH \rightarrow C_2H_5OH + HNO_2$$
$$HNO_2 + 6H \rightarrow NH_3 + 2H_2O$$
$$\overline{C_2H_5NO_2 + 6H \rightarrow C_2H_5OH + NH_3 + H_2O}$$

(3) *Action of Alkalies.* Alkyl nitrites, like other esters, are readily hydrolysed by alkalies, yielding an alkali nitrite and the corresponding alcohol, *e.g.*,

$$C_2H_5.NO_2 + NaOH \rightarrow C_2H_5OH + NaNO_2.$$

Nitro-paraffins are not decomposed by alkalies, but as already mentioned, they may form soluble metallic salts.

(4) *Action of Nitrous Acid.* Primary and secondary nitro-paraffins react with nitrous acid, yielding *nitrolic acid* and *pseudo-nitrols* respectively (*see p.* 116). Alkyl nitrites do not react with nitrous acid.

QUESTIONS

1. What are amines ? Give the various classes of amines and their general methods of preparation. How may a primary amine be obtained in a *pure* condition ?

2. Write a short account of the general properties and constitution of aliphatic amines. How are they classified, and how may the different classes be distinguished from one another ? *(Punjab, B.Sc., 1922)*

3. How would you effect the separation of a mixture of primary, secondary and tertiary amines ? *(Punjab. Inter., 1932)*

4. Compare and contrast the properties of methylamine with those of acetamide.

5. Describe the various methods oi preparing methylamine. Describe its properties and chemical reactions. How would you distinguish ammonia and methylamine in aqueous solution ? *(Unit. Prov. Inter., 1942)*

6. How can ethylamine be prepared ? Describe reaction to show its differences from ethylamine and triethylamine. How can a primary amine be separated from a secondary amine ? *(Punjab. Inter., 1945)*

7. what is the difference between an amine and an amide ? How will you distinguish one from the other ? How may acetamide be converted into methylamiue ?

8. What do you understand by Ascent and Descent of Homologous Series ? How may the following conversions be effected ? :— (*a*) Ethyl alcohol into Methyl alcohol ;(b) Methyl alcohol into ethyl alcohol ; (*c*) Acetic acid into propionic acid ; (*d*) Propionic acid into acetic acid ; (*e*) Acetamide into methylamine.

9. How would you obtain ? :—
   (*a*) Acetamide from acetic acid ;
   (*b*) Methylamine from acetamide ;
   (*c*) Methyl alcohol from methylamine ;

Give all necessary equations. *(Unit. Prov., Inter., 1927)*

10. Give the preparation and cheif properties of *nitroparaffins*. What other alkyl derivatives of nitrous acid are known, and in what respects they differ from nitroparaffins ?

11. A monoacid primary amine contains 53·3% of carbon, 15·6% of hydrogen and 31·1% of nitrogen. 0·1087 gram of its platinichloride gave 0·024 gm. of platinum on ignition. Calculate the molecular formula of the amine *(Ajmer, Inter., 1940)*

CHAPTER 18

SUBSTITUTED MONOCARBOXYLIC ACIDS

1. The compounds discussed in this chapter are derived from fatty acids by substitution in the hydrocarbon radical. Some simple examples of such substituted monocarboxylic acids are :—

Chloroacetic acid, $CH_2Cl.COOH$,

Amino-acetic acid (glycine), $CH_2(NH_2).COOH$.

Hydroxy-acetic acid (glycollic-acid), $CH_2(OH)\,COOH$.

In naming the derivatives of propionic and higher acids the position of the substituent with respect to the carboxyl group is indicated by Greek letters. Thus, propionic acid, $CH_3.CH_2COOH$, gives rise to two monohydroxy acids :—

$CH_3.CH(OH).COOH$	$CH_2(OH).CH_2.COOH$
a-Hydroxy-propionic acid (Lactic acid)	*b*-Hydroxy-propionic acid (Hydracrylic acid)

The reactions of substituted carboxylic acids may be classified under three different headings ; (1) the reactions of the carboxyl group (*p.* 169), (2) the reactions of the substituent group, and (3) decompositions involving one or both of these groups.

2. **Chloro-acetic Acid**, $CH_2Cl.COOH$, Monochloro-acetic Acid. This acid is prepared commercially by the action of chlorine on acetic acid in the presence of a catalyst (a little red phospherus or acetyl chloride) :—

$$CH_3.COOH + Cl^2 \rightarrow CH_2Cl.COOH + HCl$$

Physical Properties. Chloroacetic acid crystallizes in needless (m.p. 63°, b.p. 186°). and has a strong corrosive action on the skin. It is freely soluble in water, and the solution possesses a strong acid reaction. It is a far stronger (about 86 times) than acetic acid.

Reactions Chloro-acetic acid possesses the dual character of a carboxylic acid and an alkyl halide. Like the former, it reacts with alkalies and alcohols, yielding salts and esters ; *e.g.*,

$$CH_2Cl.COOH + NaOH \rightarrow \underset{\text{Sodium chloroacetate}}{CH_2Cl.COONa} + H_2O$$

$$CH_2Cl.COOH + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl chloroacetate}}{CH_2Cl.COOC_2H_5} + H_2O$$

It also reacts with phosphorus pentachloride, yielding chloroacetyl chloride,

$$CH_2Cl.COOH + PCl_5 \rightarrow \underset{\text{Chloroacetyl chloride}}{CH_2Cl.COCl} + POCl_3 + HCl.$$

It resembles alkyl halides (Sec. 79) in giving the following reactions, in which the halogen atom is replaced by substituents :—

(1) When *boiled* with water or an aqueous alkali, it gives hydroxyacetic acid (glycollic acid) :—

$$CH_2Cl.COOH + H.OH \rightarrow \underset{\text{Glycollic acid}}{CH_2(OH).COOH} + HCl$$

(2) When the potassium of the acid is boiled with alcoholic potassium cyanide, the chlorine atom gets replaced by the —CN group :—

$$CH_2Cl.COOK + KCN \rightarrow \underset{\text{Potassium cyanoacetate}}{CH_2(CN)COOK} + KCl$$

(3) By the action of alcoholic ammonia the halogen atom is replaced by the amino group :—

$$CH_2ClCOOK + 2NH_3 \rightarrow \underset{\text{Potassium aminoacetate}}{CH_2(NH_2)COOK} + NH_4Cl$$

(4) By heating the potassium salt with silver nitrite, the halogen atom is replaced by the nitro-group :—

$$CH_2Cl.COOK + AgNO_2 \rightarrow \underset{\text{Potassium nitro-acetate}}{CH_2(NO_2)COOK} + AgCl$$

Use. Chloro-acetic acid is employed in organic synthesis.

3. Hydroxy Monocarboxylic Acids. These are derived from fatty acid by the replacement of a hydrogen atom of the alkyl group by a hydroxyl group In naming these compounds the position of the carboxyl group is indicated by a Greek letter :—
$CH_2(OH).COOH$. Hydroxyacetic acid, are glycollic acid.
$CH_3CH(OH).COOH$ α-Hydroxypropionic, or lactic acid.
$CH_2(OH).CH_2.COOH$ β-Hydroxypropionic acid or hydracrylic acid.

Methods of Formation. The hydroxy acid can be synthesized by introducing into the molecule of a substance (1) the OH group, (2) COOH group, or (3) both the groups at the same time.

(1) *By the introduction of* OH *Group.*

(*i*) A fatty acid may be converted first into a chloro-substituted acid and the latter is then boiled with water or aqueous alkali :—

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{\text{Chlorination}} \underset{\text{Chloro-acetic acid}}{CH_2Cl\,COOH} \xrightarrow{H.OH} \underset{\text{Hydroxyacetic acid}}{CH_2(OH).COOH}$$

(*ii*) Starting with an amino acid, we can prepare a hydroxy acid by treatment with nitrous acid :

$$\underset{\text{Aminoacetic acid}}{CH_2(NH_2).COOH} + HNO_2 \rightarrow \underset{\text{Hydroxyacetic acid}}{CH_2OH.COOH} + N_2 + H_2O$$

(2) *By the Introduction of*—COOH *Group.* Hydroxy acids may be obtained by the careful oxidation of polyhydric alcohols. Thus, glycol on careful oxidation with dilute nitric acid give. glycollic acid :—

$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} + 2O \rightarrow \underset{\text{Glycollic acid}}{OH_2OH.COOH} + H_2O$$

(3) *By the Introduction of both*—OH *and*—COOH *Groups.* This is effected by the adition of hydrogen cyanide to an aldehyde or a ketone, and hydrolysing the resulting cyanohydrin ; *e g.*,

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow{+HCN} \underset{\text{Acetaldehyde cyanodydrin}}{CH_3.CH(OH)CN} \xrightarrow{H.OH} \underset{\text{Lactic acid}}{CH_3.CH(OH).COOH}$$

Physical Properties. The hydroxy monobasic acids are colourless, crystalline solids, or syrupy liquids, very readily soluble in water. Even the lower members cannot be distilled without decomposition, except under reduced pressure. They are stronger acids than the fatty acids and possess much higher boiling points.

Reactions. The hydroxy acids posses the dual character of an alcohol and a carboxylic acid. Their reactions may be studied under

three heads :—

(1) *Reactions of the* —CH *Group and Behaviour on Oxidation :*

(*i*) With acetyl chloride, they give monoacetyl derivatives, *e.g.*,

$$\underset{\text{Glycollic acid}}{CH_2(OH).COOH} + CH_3COOCl \rightarrow \underset{\text{Acetylglycollic acid}}{CH_2(O\,CO.CH_3)COOH} + HCl$$

(*ii*) On being heated with hydriodic acid, they are reduced to the corresponding fatty acids ; *e.g.*,

$$\underset{\text{Glycollic acid}}{CH_2(OH)\,COOH} + 3Cl \rightarrow \underset{\text{Acetic acid}}{CH_3.COOH} + H_2 + Cl_2.$$

(*iii*) *Hydroxy acids* containing a —CH_2OH group, on careful oxidation, give an aldedydic acid, and, on further oxydation, a dibasic acid :

$$\underset{\text{Glycollic acid}}{\begin{matrix}CH_2OH\\|\\COOH\end{matrix}} \rightarrow \underset{\text{Glyoxalic acid}}{\begin{matrix}CHO\\|\\COOH\end{matrix}} \rightarrow \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}}$$

The acids containing a $>$CHOH group, on the other hand, yield ketonic acids (compare secondary alcohols) :

$$\underset{\text{Lactic acid}}{CH_3.CH(OH)\,COOH} + O \rightarrow \underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + H_2O$$

(2) *Reactions of the Carboxyl Group.* The hydroxy acids possess the usual character of a corboxylic acid. Thus, with alkalies and alcohols they form salts and esters respectively :

$$\underset{\text{Glycollic acid}}{CH_2(OH)\,COOH} + NaOH \rightleftharpoons \underset{\text{Sodium glycollate}}{CH_2(OH).COONa} + H_2O$$

$$\underset{\text{Glycollic acid}}{CH_2(OH).COOH} + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl glycollate}}{CH_2(OH).COOC_2H_5} + H_2O$$

(3) *Reactions involving both the Hydroxyl and the Carboxyl Group.* This may take place in two ways :

(*i*) The two groups react *independently.* Thus, with phosphorus pentachloride we get a chloro acid chloride and with metallic sodium a disodio derivative :

$$CH_2(OH).COOH + 2PCl_5 \rightarrow \underset{\text{Chloroacetyl chloride}}{CH_2Cl\,CO.Cl} + 2POCl_3 + 2HCl$$

$$CH_2(OH).COOH + 2Na \rightarrow \underset{\text{Disodium glycollate}}{CH_2(ONa)COONa} + H_2$$

(*ii*) They *both react together*, with elimination of water. This occurs on heating :

$$\underset{\text{Glycollic acid (2 molecules)}}{\begin{matrix}CH_2.OH\\|\\COOH\end{matrix} + \begin{matrix}HOOC\\|\\HO.CH_2\end{matrix}} \xrightarrow{-2H_2O} \underset{\text{Glycolide}}{\begin{matrix}CH_2.O.CO\\|\quad|\\CO.\,O.\,CH_2\end{matrix}}$$

4. Glycollic Acid, $CH_2(OH)COOH$ *Hydroxyacetic Acid.* This acid occurs in unripe grapes. It is usually prepared by boiling the potassium salt of chloroacetic acid with water,

$$CH_2Cl.COOK + H_2O \rightarrow CH_2(OH).COOH + KCl,$$

evaporating the solution to dryness, and extracting the residue with acetone, which dissolves the acid, leaving behind the potassium chloride.

Glycollic acid is a colourless, crystalline and hygroscopic solid;

readily soluble in water, alcohol and acetone. Its chemical properties have already been discussed.

5. Lactic acid, $CH_3.CH(OH).COOH$ *α-Hydroxy Propionic Acid.* This acid occurs in sour milk, being produced by the *lactic fermtelntation* of milk, sugar, induced by *lactic bacilli :*

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_3H_6O_3.$$

Preparation in Laboratory. The laboratory method for preparing lactic acid consists in fermenting a 15 per cent solution of glucose by means of sour milk or old cheese, which contain plenty of lactic bacilli. To avoid butyric fermentation, the temperature is maintained at 44° —55°C. Further, since the lactic bacilli are very sensitive towards free acid, the acidity of the solution must not be allowed to go higher than 1 per cent by the gradual addition of calcium carbonate or zinc carbonate. The sparingly soluble calcium lactate or zinc lactate thus obtained is decomposed, the former with dilute sulphuric acid and the latter with hydrogen sulphide. The insoluble calcium sulphate or zinc sulphide is filtered off, and the solution evaporated. Finally, the acid is purified by distillation *in vacuo.*

Manufacture. Lactic acid is manufactured by the fermentation of raw beet-juice by means of lactic bacilli. The acidity is kept down by means of lime. Calcium lactate is decomposed with sulphuric acid, and the liquid, after filtering off calcium sulphate, is evaporated to a syrup containing 50 per cent lactic acid, in which form the acid is put on the market.

Properties. When pure, lactic acid is a colourless, crystalline, highly deliquescent solid. It is, however, ordinarily met with as a thick syrupy liquid.

Lactic acid shows the usual chemical behaviour of a hydroxy acid (*p.* 177). When heated, it yields lactide, along with other products.

$$\underset{\text{Lactic Acid (2 molecules)}}{CH_3.CH(OH).COOH} + HO.CH(CH_3).COOH \xrightarrow{-2H_2O} \underset{\text{Lactide}}{CH_3.CH.O.CO.CO.O.CH.CH_3}$$

Hence it is only under reduced pressure that the acid can be distilled without decomposition.

Constitution. From the reactions of lactic acid it follows that the compound is a hydroxy acid. Since its molecular formula is $C_3H_6O_3$, it must be either α-hydroxypropionic acid, $CH_3.CH(OH).COOH$, or β-hydroxypropionic acid, $CH_2(OH)CH_2.COOH$. The synthesis of the compound from acetaldehyde through the cyanohydrin reaction,

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow{HCN} \underset{\text{Acetaldehyde cyanohydrin}}{CH_3.CH(OH)CN} \xrightarrow{\text{Hydrolysis}} \underset{\text{Lactic acid}}{CH_3.CH(OH).COOH}$$

proves that the acid is *alpha*-hydroxypropionic acid.

Tests. (1) When lactic acid is warmed with dilute sulphuric acid (30 per cent), the odour of acetaldehyde is developed

(2) If to a few c.c.'s. of lactic acid solution 5 c.c 's. of concentrated sulphuric acid are added and then 2 or 3 drops of alcoholic

thiophine, a cherry-red colour is produced.

(3) If to a dilute solution of lactic acid concentrated sulphuric acid is added and then 2 or 3 drops of a 5 per cent solution of guaiacol, a rose-red colour is developed.

Uses. (1) Lactic acid is used, along with potassium dichromate, for mordanting wool. its chief advantage being its high solubility and absence of corrosive action.

(2) It is also employed in tanning, for removing lime from pelts.

(3) Its calcium salt is used in medicine, to supply the deficiency of calcium in blood.

6. Amino Acids. Amino acids are derived from the carboxylic acids by the replacement of the hydrogen of the hydrocarbon radical by an amino group $—NH_2$. As in the case of the hydroxy acids they are designated as α-, β-, and γ- substituted acids according to the position of the $—NH_2$ group with respect to the carboxyl group:—

$CH_2(NH_2).COOH$, Amino-acetic acid.

$CH_3.CH(NH_2).COOH$. α-Amino-propionic acid.

$CH_2(NH_2).CH_2.COOH$, β-Amino-propionic acid.

Amino-acids are of great physiological importance, since they constitute the ultimate products of hydrolysis of proteins.

Methods of Preparation. (1) By the action of ammonia on halogen substituted acids (compare preparation of amines) : —

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + H.NH_2 \rightarrow \underset{\text{Amino-acetic acid}}{CH_2(NH_2).COOH} + HCl.$$

(2) When an aldehyde or a ketone is treated with hydrogen cyanide, and the resulting cyanohydrin is allowed to react with ammonia, we get an amino-nitrile This, on being hydrolysed, yields an α-amino acid :

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow{+HCN} \underset{\substack{\text{Acetaldehyde}\\ \text{cyanohydrin}}}{CH_3CH<\begin{matrix}OH\\CN\end{matrix}} \xrightarrow{NH_3} \underset{\substack{\text{Nitrile of } \alpha\text{-amino}\\ \text{propionic acid}}}{CH_3.CH<\begin{matrix}NH^2\\CN\end{matrix}}$$

$$\xrightarrow[\text{H.OH}]{} CH_3.CH<\begin{matrix}NH_2\\COOH\end{matrix}$$

α-Aminopropionic acid

Note. The conversion of an alcehyde or a ketone into the nitrile of the α-amino acid can be effected in one step by using ammonium cyanide or, even more conveniently, by using the mixture of potassium cyanide and ammonium chloride in aqueous solution.

(3) Amino-acids are largely prepared by the hydrolysis of proteins by means of mineral acids or barium hydroxide

Physical Properties Amino acids are generally crystalline substanc-s of sweet taste. They are readily soluble in water, but insoluble in alcohol and ether.

Reactions. (1) *Salt Formation with Acids and Alkalies.* By virtue of the presence in the molecule of both the $—NH_2$ group and the —COOH group, an amino acid can react with acids as well as with alkalies :

$$\underset{\text{Amino-acetic acid}}{CH_2(NH_2).COOH} + HCl \rightarrow \underset{\text{Hydrochloride of amino-acetic acid}}{CH_2(NH_2.HCl).COOH}$$

$$\underset{\text{Amino-acetic acid}}{CH_2(NH_2).COOH} + KOH \rightarrow \underset{\substack{\text{Potassium salt of}\\ \text{amino-acetic acid}}}{CH_2(NH_2).COOK} + H_2O$$

But, since the basic nature of the amino group is counter-balanced by the acidic nature of the carboxyl group, the amino acids are neutral towards litmus.

(2) *Esterification.* Like other carboxylic acids, the acids of this group form esters with alcohols. To prepare an ester, hydrochloric acid gas is passed through a mixture of an amino-acid and an alcohol. The product consists of the hydrochloride of the ester, *e. g.*, $CH_2(NH_2HCl).COOH_2H_5$. This is decomposed by means of an alkali to get the free ester. Unlike the acids themselves, the ester can be distilled without decomposition. This fact was employed by Fischer to effect the separation of a mixture of amino acids.

(3) Amino acids, like other compounds containing the $—NH_2$ group react with nitrous acid to give a hydroxy acid and free nitrogen :

$$CH_2(NH_2).COOH + O:N.OH \rightarrow CH_2(OH).COOH + N_2 + H_2O.$$

The reaction is employed for the estimation of amino acids.

Constitution. According to the modern view, the molecule of and amino acid does not contain the $—NH_2$ and the —COOH groups in the free state as in formula I originally given to these compounds. It is assumed that the hydrion of the carboxyl group migrates to the basic $—NH_2$ group, which thereby becomes the positive ion $—NH_3^+$. At the same time, the carboxyl group is transformed into the negative ion $—CO^-$. These two ions form part of the seme molecule, and bind each other by an electrovalency, as show in formula II below :—

$CH_2.NH_2$ | $COOH$ — Formula I

$CH_2.NH_3^+$ | COO^- — Formula II

The latter formula is sometimes referred to as the **betain formula** for amino acids. Amino-acids are thus regarded as intramolecular salts. The fact that amino-acids are readily soluble in water, slightly so in alcohol, and insoluble in ether is in agreement with their saline character (Formula II).

7. Amino acetic Acid, *Glycine*, CH_2NH_2 | $COOH$

This is the simplest of the amino-acids, and occurs in the urine of the horse as **hippuric** acid *benzoylglucine*, $C_6H_5.CO.NH.CH_2.COOH$, from which it may be liberated by hydrolysis with hydrochloric acid :

$$C_6H_5CO.NH.CH_2.COOH \xrightarrow{HOH} C_6H_5.COOH + NH_2CH_2.COOH$$

Hippuric acid → Benzoic acid + Aminoacetic acid

Preparation. (1) *From Chloroacetic Acid.* The most convenient method for the preparation of aminoacetic acid in the laboratory is by interaction of monochloroacetic acid and ammonia :—

$$CH_2Cl.COOH + NH_3 \rightarrow CH_2(NH_2).COOH + HCl.$$

Expt. 1. *Preparation of Amino acetic acid.*

Ammonium hydroxide (*sp. gr.* 0·88), 300 c. c.

Monochloroacetic acid, 25 grams.

Water, 25 c.c.

Place the ammonium hydroxide in a beaker, and slowly drop into it the chloroacetic acid dissolved in water. Keep the ammonia well stirred throughout the addition of chloroacetic acid. Let the liquid stand for 24 hours, and then transfer

it to a dish, and evaporate it down to a small bulk. If there is still any smell of ammonia, remove it by passing in steam.

Add cupric carbonate to the hot liquid, a little at a time, until some remains undissolved. Filter the solution, and evaporate it to crystallization. Allow it to cool, and filter off the blue-coloured crystals of cupric aminoacetate, and wash with dilute alcohol.

Dissolve the crystals in hot water, and pass in hydrogen sulphide, until the blue colour of the solution has disappeared. Filter off the cupric sulphide, and evaporate the solution of aminoacetic acid to a small bulk. On allowing the solution to cool, the acid will crystallize out.

(2). *From Glue.* Glue is boiled with dilute sulphuric acid, till completely hydrolysed. From the resulting solution, **amino-acetic acid** is separated by means of the cupric derivative as in Expt. 1.

Properties. Aminoacetic acid crystallizes from aqueous solution in colourless prisms (Fig. 1). It possesses sweet taste, and melts at 232°

Fig. 1. Crystals of Amino-acetic acid.

For the *reactions* and the *constitution* of the acid refer *pp.* 179-180. The fact that the acid is readily soluble in water, slightly so in alcohol, and insoluble in ether classes it with salts. This agrees with Formula II given on *p.* 180.

The most characteristic metallic salts of this acid is the **cupric salt**, $(NH_2.CH_2.COO)_2Cu.H_2O$, which crystallizes in dark-blue needles.

The **ethyl ester**, $NH_2.CH_2.COOC_2H_5$, boils at 52° under a pressure of 10 mm. On being reduced in neutral solution by means of sodium amalgam, the ester yields **amino-acetaldehyde**.

QUESTIONS

1. Give the preparation and chief reactions of chloroacetic acid. To what use is this acid put ?

2. How would you convert a fatty acid into the corresponding hydroxy acid and *vice versa ?* *(Punjab, Inter., 1925)*

3. Discuss the general methods of preparation and the chief reactions of hydroxy monobasic acids. Give two examples of the acids of this group.

4. Starting from the elements, describe a scheme for the synthesis of lactic acid. How is it manufactured ? By what reactions would you show its dual character and establish, its constitution ? *(Punjab, Inter., 1944)*

5. Discuss the chief methods, preparation and properties of aminoacids. *(Punjab, Inter., 1925)*

6. Describe the preparation and chief properties of amino-acetic acids and discuss its constitution.

CHAPTER 19

POLYHYDRIC ALCOHOLS

1. Polyhydric alcohols are derived from paraffin hydro-carbons by the replacement of two or more hydrogen atoms by hydroxyl groups. Except in rare cases the members of this series contain the hydroxyl groups linked to *different* carbon atoms the compounds containing more than one hydroxyl group linked to the *same* carbon atom, being, as a rule, unstable.

Dihydric alcohols or glycols are usually named after the corresponding olefines. The Geneva names for dihydric alcohols are obtained by adding the termination *diol* to the name of the corresponding paraffin hydrocarbon. Similarly, for the trihydric alcohols the termination *triol* is employed.

2. Ethylene Glycol, $\begin{matrix}CH_2OH\\|\\CH_2HO\end{matrix}$, *Glycol* or *Ethane-diol.* This is the simplest of the dihydric alcohols. In its preparation and general chemical behaviour, glycol resembles ethyl alcohol.

Laboratory Preparation. Ethylene glycol is prepared by the hydrolysis of ethylene dibromide, $C_2H_4Br_2$. This is boiled with a solution of potassium carbonate under a reflux condenser, until the oily drops (of ethylene dibromide) have completely disappeared :—

$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + 2H.OH \rightleftharpoons \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 2HBr$$

$$2HBr + K_2CO_3 \rightarrow 2KBr + H_2O + CO_2$$

The resulting solution is slowly evaporated on a water-bath to remove most of the water. The semi-solid residue is extracted with alcoholic ether, which dissolves the glycol, leaving behind potassium bromide. The liquid is then filtered and fractionally distilled, in order to isolate glycol.

Manufacture. Glycol is prepared on a large scale from ethylene contained in the petroleum-cracking gas. The gas is passed in to aqueous hypochlorous acid when ethylene chlorohydrin is produced.

$$\begin{matrix}CH_2\\\|\\CH_2\end{matrix} + HO.Cl \rightarrow \begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix}$$

Ethylene — Ethylene glycol

The ethylene chlorohydrin is separated by steam distillation and, then hydrolysed with sodium bicarbonate solution.

$$\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix} + H.OH \rightarrow \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + HCl$$

Ethlene glycol

Properties. Glycol is a colourless, syrupy liquid boiling at 197.5°.

Glycol possesses the chemical behaviour of a diprimary alcohol :

(1) It reacts with sodium to give monosodium and disodium glycolates and with phosphorus to give ethylene chloride :

$$\underset{\text{Glycol}}{CH_2OH\text{-}CH_2OH} \xrightarrow{Na} \underset{\text{Monosodium glycolate}}{CH_2ONa\text{-}CH_2OH} \xrightarrow{Na} \underset{\text{Disodium glycolate}}{CH_2ONa\text{-}CH_2ONa}$$

$$\underset{\text{Glycol}}{CH_2OH\text{-}CH_2OH} + 2PCl_5 \rightarrow \underset{\text{Ethylene chloride}}{CH_2Cl\text{-}CH_2Cl} + 2POCl_3 + 2HCl$$

(2) *Esterification.* Glycol reacts with acid to form two series of esters, normal esters and the alcohol-esters ; *e g.*

$$\underset{\text{Glycol}}{CH_2OH\text{-}CH_2OH} \xrightarrow{CH_3COOH} \underset{\text{Glycol mono-acetate}}{CH_2.O.COCH_3\text{-}CH_2OH} \quad \underset{\text{Glycol di-acetate}}{CH_2O\,COCH_3\text{-}CH_2.O.COCH_3}$$

When heated with hydrogen chloride or bromide, only one of the hydroxyl groups is replaced by halogen, resulting in the formation of chloro and bromo-hydrins :—

$$\underset{\text{Glycol}}{CH_2OH\text{-}CH_2OH} + HCl \rightarrow \underset{\text{Glycol chlorohydrin (or Ethylene chlorohydrin)}}{CH_2Cl\text{-}CH_2OH} + H_2O$$

(3) *Oxidation.* On being carefully oxidized with nitric acid, glycol gives the following products :

$$\underset{\text{Glycol}}{CH_2OH\text{-}CH_2OH} \rightarrow \underset{\text{Glyoxal}}{CHO\text{-}CHO} \rightarrow \underset{\text{Glyoxalic acid}}{CHO\text{-}COOH} \rightarrow \underset{\text{Oxalic acid}}{COOH\text{-}COOH}$$

$$\underset{\text{Glycol}}{CH_2OH\text{-}CH_2OH} \rightarrow \underset{\text{Glycollic acid}}{CH_2OH\text{-}COOH}$$

Synthesis and Constitution. Glycol can be synthesized from ethylene through ethylene dibromide (*p.* 182). This synthesis proves its constitution, which is fully supported by the entire chemical behaviour of glycol.

Uses. Glycol is used as an anti-freeze compound for automobile and aeroplane radiators. It is also used as a substitute for glycerol in anti-freeze dynamite.

3. **Glycerol,** $CH_2OH\text{-}CHOH\text{-}CH_2OH$, *Glycerine, Propane-triol.* This is the most important trihydric alcohol. It occurs in nature in fats and oils, which are mixtures of glycerol with higher fatty acids and unsaturated acids. Glycerol is also present in small quantities in fermented sugar solution, and in minute traces in the blood.

Manufacture. Glycerol is chiefly obtained from fats and oils. Hydrolysis of fats and oils is carried out on a large scale for two different purposes ; (1) for the manufacture of soap, and (2) for the manufacture of stearine. The *spent lye* and the *sweet water*, obtained as by-products in these industries, constitute the most important sources of commercial glycerol. Glycerol has also been obtained from sugar by fermentation.

(1) ***From Spent Lye.*** The spent lye from the soap kettle is run into an iron tank to cool Here most of the dissolved soap and heavy impurities separate out The clear liquid is then run into a "treating tank" (Fig. 1), provided with an open steam coil for heating. Three-fourths of the free alkali present in the lye is neutralized by means of hydrochloric acid, and then a calculated amount of basic ferric sulphate (got by treating finely powdered iron ore with an insufficient quantity of H_2SO_4) is added. This destroys the remaining alkali,

$$6NaOH + Fe_2(SO_4)_3 \rightarrow 2Fe(OH)_3 + 3Na_2SO_4,$$

and precipitates the fatty acids present as insoluble iron soaps.

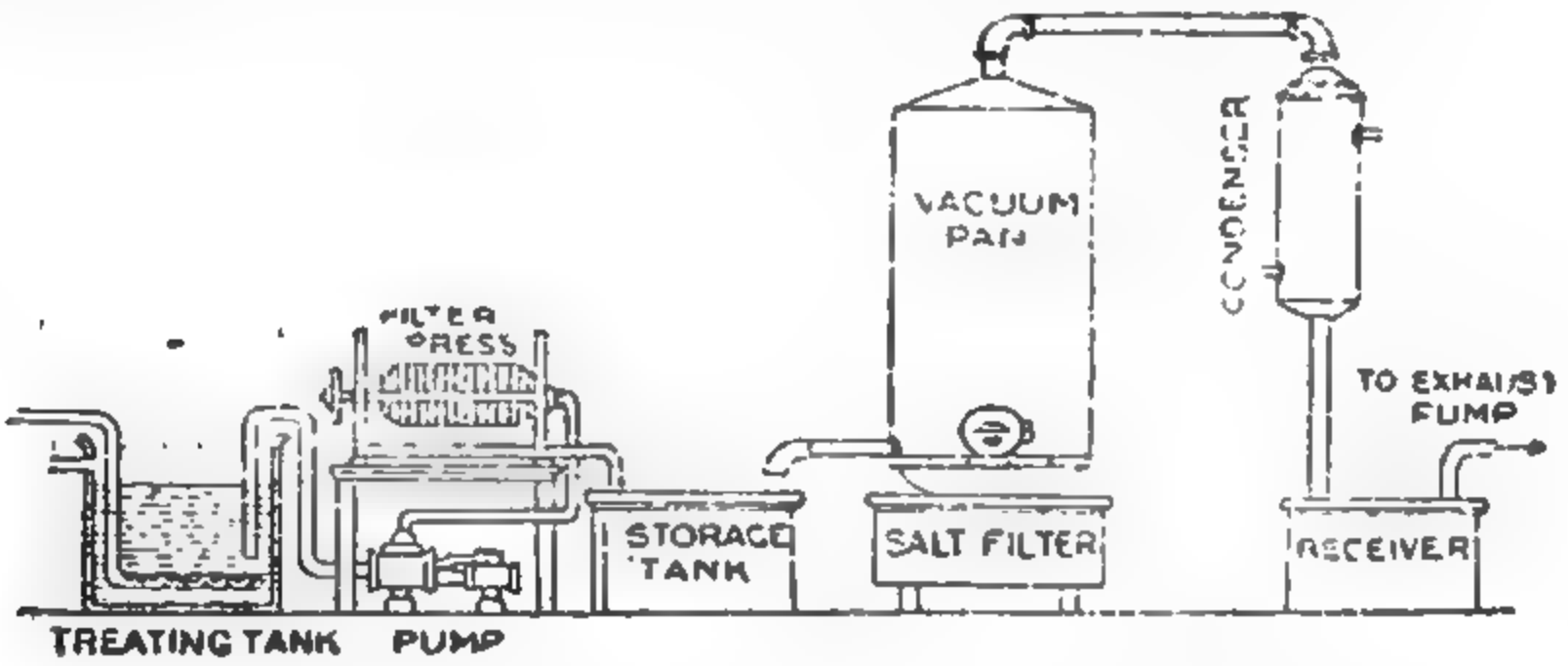


Fig. 1. Plant for Recovery of Glycerol from Spent Lye.

The gelatinous precipitate, consisting of hydrous ferric oxide and iron soaps, carries down with it the albuminous matter that the lye may contain.

The lye is then forced, by means of a pump, through a filter press, which retains the precipitate, while the clear liquid is run into a storage tank. From here the liquid is pumped into a steam-heated vacuum pan, consisting of a sheet-iron boiler, heated internally by closed steam pipes, and connected to a vacuum pump. The latter serves to maintain a low pressure inside the evaporator. Under the reduced pressure, the water repidly boils off, while glycerol remains. During the concentration, the salts crystallize out and settle down at the bottom of the pans, whence they are periodically removed.

The crude glycerol obtained as above, still contains about 20 per cent of water and certain impurities. It is decolorized by filtration through animal charcoal, and then purified by distillation with superheated steam. The aqueous solution thus obtained is concentrated in steam-heated vacuum pans, when perfectly colourless glycerol is obtained.

(2) ***From Sweet Water.*** The *sweet water*, obtained in the hydrolysis of fats and oils by means of superheated steam, contains volatile fatty

acids in addition to glycerol and water. It, is therefore, mixed with a calculated quantity of sodium carbonate. to convert the acids into non-volatile sodium salts. The liquid is then concentrated in vacuum pans, filtered through animal charcoal, distilled in superheated steam, and finally concentrated to the required consistency in multiple-effect vacuum pan.

(3) ***From Sugar.*** During fermentation of sugar by means of yeast appreciable quantities of glycerol are produced along with ethyl and other alcohols. The proportion of glycerol in the product is considerably increased, while that of alcohol is decreased, if sodium sulphite, Na_2SO_3, be added to the fermenting liquid. On this fact is based an important process for the manufacture of glycerol. The yield of glycerol by this method is from 15 to 20 per cent of the sugar employed.

Physical Properties. Glycerol is a colourless, syrupy liquid which, when pure, freezes to a crystalline solid, melting at 17°C. When perfectly free from impurities, it boils without decomposition under the atmospheric (boiling point, 290°). If, however, it contains traces of salts, it can only be distilled, without decomposition under reduced pressure, or in a current of steam. In common with other polyhydric compounds, glycerol has a sweet taste. It is completely soluble in water and alcohol, but not in ether.

Chemical Properties. The constitutional formula of glycerol is $CH_2OH.(CHOH.CH_2OH$. Its reactions may, therefore, be discussed under the following heads :—

(1) *Reactions of the Hydroxyl Group.* Like other compounds containing hydroxyl group, glycerol readily reacts with metallic sodium and phosphorus pentachloride. With the latter reagent, all the three hydroxyl groups, are replaced by chlorine, giving glycerol trichloride :—

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3PCl_5 \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \\ \text{Glyceryl trichloride} \end{array} + 3POCl_3 + 3HCl$$

With metallic sodium, a monosodium derivative is produced at lower and a disodium derivative at higher temepratures :—

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} \xrightarrow{Na} \begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Monosodium glycerolate} \end{array} \xrightarrow{Na} \begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \\ \text{Disodium glycerolate} \end{array}$$

The hydrogen atom of the third hydroxyl group is not replaced by sodium by any ordinary treatment.

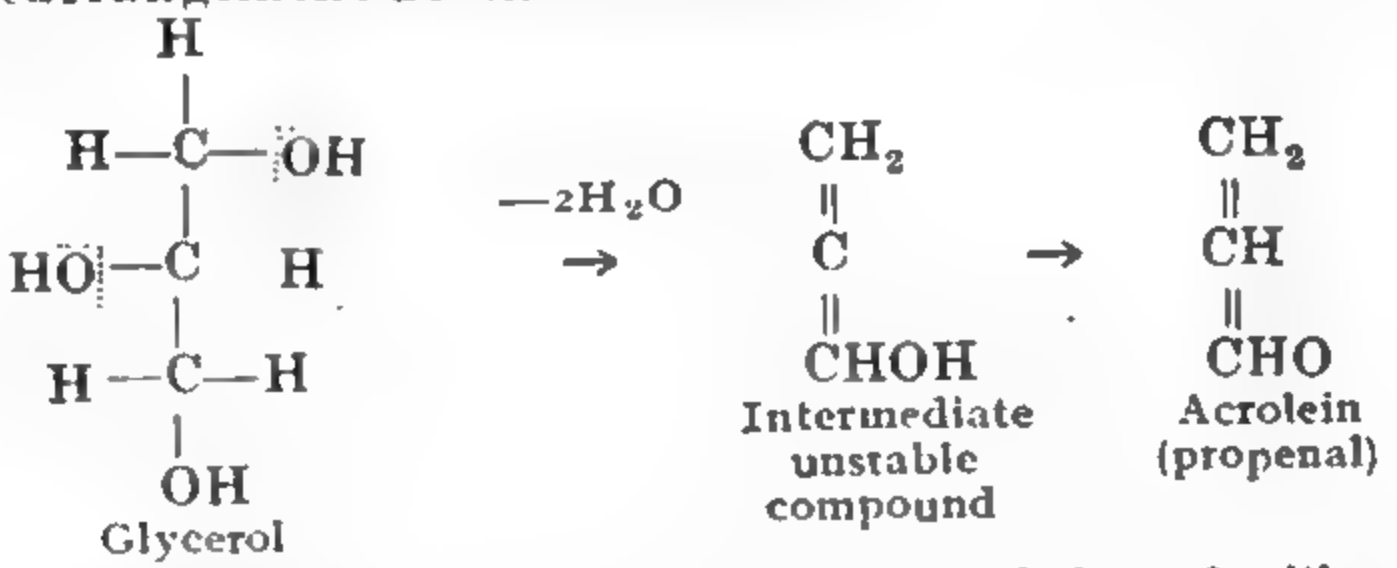
(2) *Esterification.* Glycerol, like ethyl alcohol, forms esters with organic as well as inorganic acids. Thus, fats and oils are the glycerides of fatty acids. The most important ester of glycerol with a mineral acid is **glyceryl trinitrate**, $C_3H_5(NO_3)_3$, which is erroneously called "**nitroglycerine**", and finds extensive use as an explosive.

It is prepared by the interaction of glycerol and nitric acid in the presence of sulphuric acid, the temperature being kept at 15° to 22°C :—

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3HNO_3 \rightleftharpoons \begin{array}{l} CH_2.NO_3 \\ | \\ CH.NO_3 \\ | \\ CH_2.NO_3 \\ \text{Nitroglycerine} \end{array} + 3H_2O$$

(3) *Reactions of $-CH_2OH$ and $>CHOH$ Groups.* The glycerol molecule contains two primary and one secondary alcohol groups. Hence, on oxidation, it can form a large number of products, theoretically eleven. On careful oxidation with bromine or dilute nitric acid, it is converted into "glycerose", which is a mixture consisting mainly of **dihydroxyacetone,** $CH_2OH.CO.CH_2OH$, together with smaller quantities of glyceric aldehyde, $CH_2OH.CHOH.CHO$. Other important oxidation products of glycerol are : glyceric acid, $CH_2OH.CHOH.COOH$; tartronic acid, $COOH.CHOH.COOH$ and mesoxalic acid, $COOH.CO.COOH$.

(4) *Action of Dehydrating Agents.* When glycerol is distilled with potassium hydrogen sulphate, or when its vapour is passed over heated magnesium sulphate, it loses 2 molecules of water, giving the unsaturated aldehyde acrolein. The reaction may be represented as taking place in two stages, the unsaturated alcohol first produced undergoing rearrangement as shown below :



Expt. 1. *Tests of Glycerol.* (1) Heat a few drops of glycerol with potassium hydrogen sulphate or phosphorus pentoxide in a test-tube ; pungent irritating vapour of acrolein is evolved.

(2) *Dunstan's test.* To a 5 per cent solution of borax, rendered pink with phenolphthalein, gradually add about 20 per cent aqueous solution of glycerol. Notice that the red colour is discharged. Now boil the solution ; the red colour returns, provided glycerol has not been used in excess.

Synthesis. Glycerol has been synthesized from acetic acid, which may be built up from its elements in a number of ways, *e.g.*,

$$C + H \xrightarrow[\text{combination}]{\text{Direct}} \underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[\text{in the presence of HgO}]{\text{Combination with water}} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

Starting with acetic acid, Friedel and Silva obtained glycerol through the following series of reactions :—

$$CH_3COOH \xrightarrow[\text{of Ca-salt}]{\text{Distillation}} CH_3.CO.CH_3 \xrightarrow{\text{Reduction}} CH_3CHOH.CH_3$$
Acetic acid — Acetone — Isopropyl alcohol

$$\xrightarrow{H_2SO_4} CH_3.CH=CH_2 \xrightarrow{Cl_2} CH_3.CHCl.CH_2Cl$$
Propylene — Propylene chloride

$$\xrightarrow{ICl} CH_2Cl.CHCl.CH_2Cl \xrightarrow[\text{Hydrolysis}]{} CH_2OH.CHOH.CH_2OH$$
1 : 2 : 3-Trichloropropane — Glycerol

Constitution. From the above synthesis it follows that glycerol is **1 : 2 : 3-trihydroxypropane**. This view is fully supported by its reactions.

Uses. (1) The chief use of glycerol is in the manufacture of nitroglycerine.

(2) On account of its non-drying character, glycerol is used for making non-drying stamp colours, shoe blacking, for filling gas meters, and also for preserving such articles of food as require to be kept moist (*e.g.*, fruits). It is also used in the manufacture of toilet soaps, cosmetics and skin preparations.

(3) On account of its high viscosity, glycerol is used as a lubricant for watches and clocks, and also for giving body to wines and liqueurs.

QUESTIONS

1. Describe the preparation, chief properties and uses of ethylene glycol.
2. Give the preparation on a large scale, properties and uses of the most important trihydric alcohol which you know. (*P.U. Inter., 1929*)
3. How may glycerol be synthesized? What evidence have we as to the structure of its molecule? (*Punjab, Inter., 1928*)
4. Give the chemistry of the synthesis of glycerol from its elements. How does glycerol react with (*a*) concentrated nitric acid, (*b*) oxalic acid, and (*c*) concentrated sulphuric acid? (*East Punjab, 1948*)
5. Give a brief account of the manufacture of glycerine, and describe the action of (*a*) heat, (*b*) oxidizing agents, (*c*) hydrochloric acid, and (*d*) oxalic acid, on it. (*Punjab., Inter., 1940*)
6. How would you synthesise glycerol from its elements? What products are formed when glycerol is (*a*) nitrated, (*b*) dehydrated, and (*c*) oxidised? (*Punjab Inter., 1948*)

CHAPTER 20

POLYBASIC ACIDS

1. Acids of the Oxalic Series. There are many series of polybasic acids derived from aliphatic hydrocarbons. The **saturated dibasic acids** have the general formula $C_nH_{2n}(COOH)_2$. The first three members of this series are:

Acid	Formula	Melting Point
Oxalic acid,	HOOC.COOH	184°
Malonic acid,	$HOOC.CH_2.COOH$	136°
Succinic acid,	$HOOC.CH_2.CH_2.COOH$	183°

The acids of this series can be synthesized by methods similar to those used for the monobasic acids. They are all crystalline solids, readily soluble in water, and are stronger than the fatty acids. They show the usual properties of the carboxyl group, and like the inorganic dibasic acids, form two series of salts and esters:

The action of heat on the various members of the series depends on the number of carbon atoms separating the two carboxyl groups. When the two carboxyls are directly linked together, as in oxalic acid, or when they are separated by not more than one carbon atom, as in malonic acid and its alkyl derivatives, decomposition occurs with the production of carbon dioxide and a fatty acid ; *e. g.*,

$$H\,\ddot{O}\ddot{O}\ddot{C}\text{-}COOH \rightarrow H.COOH + CO_2$$

Oxalic acid — Formic acid

$$H\,OOC.CH_2.COOH \rightarrow CH_3.COOH + CO_2$$

Malonic acid — Acetic acid

On the other hand, the members in which the two carboxyls are separated by two, three or four carbon atoms, lose a molecule of water yielding an **inner anhydride** ; *e. g.*,

$$\begin{matrix} CH_2.COOH \\ | \\ CH_2.COOH \end{matrix} \rightarrow \begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>O + H_2O$$

Succinic acid — Succinic anhydride

2. Oxalic Acid, *Ethane Diacid*, $\begin{matrix} COOH \\ | \\ COOH \end{matrix}$. This acid occurs as the potassium hydrogen salt of the *oxalis* and *rumex* familes.

Synthesis. Oxalic acid may be synthesized :—

(1) By the oxidation of ethylene glycol,

$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 4O \rightarrow \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2H_2O$$

Ethylene glycol — Oxalic acid

(2) By allowing the solution of cyanogen in water to stand :

$$\begin{array}{l}CN\\|\\CN\end{array} + 4H_2O \rightarrow \begin{array}{l}COONH_4\\|\\COONH_4\end{array} \rightarrow \begin{array}{l}COOH\\|\\COOH\end{array} + 2NH_3.$$

Cyanogen — Ammonium oxalate — Oxalic acid

Laboratory Preparation. Oxalic acid is prepared in the laboratory by the oxidation of cane-sugar by means of concentrated nitric acid. The oxidation proceeds very vigorously and abundant nitrous fumes are evolved :

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O$$

$$C_{12}H_{22}O_{11} + 18O \rightarrow 6C_2H_2O_4 + 5H_2O$$

Cane-sugar

Expt. 1. *Preparation of Oxalic acid*:—

Cane-sugar, 50 gm.
Concentrated nitric acid, 150 c.c.

The nitric acid is placed in a large flask, and the sugar is added. The flask is heated on a water-bath in a fume closet, until the reaction begins, after which it is allowed to proceed without the application of heat. When the reaction has moderated, the liquid is transferred to a dish and concentrated to a small bulk by evaporation on a water-bath. On being allowed to cool, the concentrated solution deposits colourless crystals of oxalic acid, $(COOH)_2.2H_2O$. The acid is obtained pure by crystallization from hot water.

Commercial Preparation. (1) *From Sawdust.* Oxalic acid is prepared on a large scale by saw-dust with a fusion mixture of caustic soda, and caustic potash, at the point of fusion (200-220°C.), in shallow iron pans. The fused mass, which contains sodium and potassium oxalates, is extracted with water. Milk of lime is added to the solution to precipitate oxalic acid as calcium oxalate. The latter is filtered, washed and then decomposed by means of a calculated amount of sulphuric acid :—

$$(COO)_2Ca + H_2SO_4 \rightarrow CaSO_4 + \begin{array}{l}COOH\\|\\COOH\end{array}$$

Calcium sulphate is filtered off, and the solution is evaporated to obtain crystals of oxalic acid.

(2) *From Sodium Formate.* When sodium formate (page 141) is heated rapidly, it loses hydrogen with the formation of sodium oxalate :-

$$2.H.COONa \rightarrow (COONa)_2 + H_2$$

The sodium salt is converted into the calcium salt by double decomposition with calcium chloride. From the calcium salt the free acid is obtained as in method (1).

Physical Properties. Oxalic acid crystallizes with two molecules of water. The hydrated acid melts at 101° and the anhydrous acid at 190°. It is fairly soluble in water, the saturated solution at the ordinary temperature being about 2N.

Reactions. The reactions of oxalic acid may be discussed under three different headings :—.

(1) *Acidic Character.* Oxalic acid contains two carboxyl groups, and shows the typical properties of an acid. It forms two series of salts and esters ; *e. g.*,

$$\begin{array}{l}COOH\\|\\COOH\end{array} + NaOH \rightarrow \begin{array}{l}HOONa\\|\\COOH\end{array} + H_2O$$

Acid sodium oxalate

$$\begin{array}{l}\mathrm{COONa}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{NaOH} \rightarrow \begin{array}{l}\mathrm{COONa}\\ |\\ \mathrm{COONa}\end{array} + \mathrm{H_2O}$$

Normal sodium oxalate

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{C_2H_5OH} \rightleftharpoons \begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H_2O}$$

Ethyl hydrogen oxalate

$$\begin{array}{l}\mathrm{COOH_2H_6}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{C_2H_5OH} \rightleftharpoons \begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{H_2O}.$$

Diethyl oxalate

(2) *Decompositions.* (*i*) When heated alone, oxalic acid yields formic acid and carbon dioxide :—

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \rightarrow \mathrm{H.COOH} + \mathrm{CO_2}$$

(*ii*) When heated with glycerol, it gives the same two products glycerol monoformate being formed as an intermediate product (*p.* 174).

(*iii*) When heated with a dehydrating agent, such as concentrated sulphuric acid or acetic anhydride, it decomposes into carbon dioxide, carbon monoxide and water :—

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \rightarrow \mathrm{CO_2} + \mathrm{CO} + \mathrm{H_2O}$$

The reaction is utilized in preparing carbon monoxide in the laboratory.

(3) *Oxidation.* When treated with potassium permanganate in the presence of dliute sulphuric acid at about 60°, oxalic acid is readily oxidized.

$$2\mathrm{KMnO_4} + 3\mathrm{H_2SO_4} \rightarrow 2\mathrm{K_2SO_4} + 2\mathrm{MnSO_4} + 3\mathrm{H_2O} + 5\mathrm{O}$$

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{O} \rightarrow 2\mathrm{CO_2} + \mathrm{H_2O} \qquad [\times 5]$$

$$2\mathrm{KMnO_4} + 5(\mathrm{COOH})_2 + 3\mathrm{H_2SO_4} \rightarrow \mathrm{K_2SO_4} + 2\mathrm{MnSO_4} + 8\mathrm{H_2O} + 10\mathrm{CO_2}$$

The reaction is made use of in volumetric analysis ; the manganous sulphate, produced in the reaction, acts as an autocatalyst.

Expt. 2. *Test of Oxalic Acid and Oxalates.* (1) Heat the acid in a dry test tube. Decomposition with evolution of CO,CO_2 and and formic acid vapour (characteristic odour), takes place, but there occurs no charring (distinction from tartaric and citric acids).

(2) Heat with concentrated sulphuric acid. The substance dissolves, giving off CO and CO_2; but there occurs no charring (distinction from tartaric acid).

(3) Drop potassium permanganate solution into a hot solution of the substance, acidified with sulphuric acid; decolorization with evolution of CO_2.

(4) Add silver nitrate solution to a *neutral* solution of the substance ; white precipitate, soluble in dilute ammonia. On warming the solution, no reduction occurs (distinction from tartaric acid).

(5) Add calcium chloride solution to a *neutral* solution of substance; white crystalline precipitate, insoluble in acetic acid.

(1) **Uses** Oxalic acid (also its antimony salt) is used as a mordant in dyeing and calico-printing.

(2) The acid is employed in the manufacture of inks and certain coal-tar dyes.

(3) It is also used for whitening leather and for bleaching and cleaning straw.

(4) Salts of oxalic acid find many minor uses in the arts (*see* below).

3. Salts of Oxalic Acid. Only ammonium and alkali oxalates are soluble in water Sodium oxalate, $(COONa)_2$, can be readily obtained pure and is used as a standard in volumetric analysis.

There are three oxalates of potassium. (*i*) the normal salt, (*ii*) the acid salt, and (*iii*) **potassium tetroxalate,** a compound formed by the combination of a molecule of the free acid with a molecule of the acid salt. It is represented by the formula $KHC_2O_4.H_2C_2O_4.2H_2O$ and is employed under the name of **salt of sorrel,** for removing ink and rust stains.

Expt. 3. Stain a piece of cloth with blue-black ink. Steep it for some time in a hot, strong solution of potassium tetroxalate, then, in very dilute ammonia, and finally rinse with water. Repeat the experiment if necessary, until the ink is completely removed

Calcium oxalate, CaC_2O_4, H_2O is insoluble in water or acetic acid, and is used for the detection and estimation of calcium and soluble oxalates.

Ferrous oxalate, which can be obtained as a yellow powder by precipitation, is used as a "developer" in photography.

Potassium ferric oxalate, $K_3Fe(C_2O_4)_3$ is used in *platinum printing.* This is based on the reduction of the salt to potassium ferrous oxalate on exposure to sunlight;

$$2K_3Fe(C_2O_4)_3 \rightarrow 2K_2Fe(C_2O_4)_2 + K_2C_2O_4 + 2CO_2$$

The printing-out paper prepared with potassium ferric oxalate is covered with thetphotographic negative and exposed to sunlight. The paper is then immersed in plainum chloride solution when ferrous oxalate, formed during exposure, reduces the solution, depositing metallic platinum on parts effected by the light.

4. Derivatives of Oxalic Acid :—

Dimethyl oxalate, $\begin{matrix}COOCH_3\\|\\COOCH_3\end{matrix}$ is obtained by passing dry hydrogen chloride into a hot solution of anhydrous oxalic acid in methyl alcohol. It is a crystalline solid (m.p. 51° ; b.p.162°).

Diethyl oxalate, $\begin{matrix}COOC_2H_5.\\|\\COOC_2H_5\end{matrix}$, is prepared in the same manner as the methyl ester. It is a liquid boiling at 186°.

Oxalyl chloride, $\begin{matrix}COCl\\|\\COCl\end{matrix}$, is obtained by the action of phosphorus pentachloride on anhydrous oxalic acid. It is a liquid boiling at 64°.

5. Malonic Acid. $CH_2<^{COOH}_{COOH}$. This acid occurs in beet root. It is prepared from chloroacetic acid by the cyanide process:

$$CH_2<^{Cl}_{COOH} \xrightarrow{KCN} CH_2<^{CN}_{COOH} \xrightarrow{H_2O} CH_2<^{COOH}_{COOH}$$

Chloroacetic acid — Cyanoacetic acid — Malonic acid

Malonic acid, like oxalic acid, is a colourless crystalline solid readily soluble in water. When heated, it loses a molecule of carbon dioxide, yielding acetic acid :—

$$CH_2{<}^{COOH}_{COOH} \rightarrow CH_3COOH + CO_2$$

The diethyl ester of malonic acid, known as malonic ester is much used in organic synthesis.

6. Succinic Acid. $\begin{matrix}CH_2.COOH\\|\\CH_2.COOH\end{matrix}$. This acid occurs in amber (Lat. *succinum*), from which source it is prepared by dry distillation. It may be synthesized from ethylene bromide a shown below :—

$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} \xrightarrow{KCN} \begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix} \xrightarrow{H.OH} \begin{matrix}CH_2.COOH\\|\\CH_2.COOH\end{matrix}$$

Ethylene bromide — Etylene cyanide

The synthesis proves the constitution of the acid.

Properties. (1) Succinic acid is a colourless, crystalline solid (m.p. 185°). It sublimes readily, giving off irritating vapour.

(2) When distilled, it is partially converted into **succinic anhydride** :—

$$\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix} \rightarrow \begin{matrix}CH_2.CO\\|\\CH_2.CO\end{matrix}\!\!>\!CO + H_2O$$

Succinic anhydride

(3) When the ammonium salt of the acid is heated it gives the closed chain-compound succinimide.

$$\begin{matrix}CH_2.COONH_4\\|\\CH_2.COONH_4\end{matrix} \rightarrow \begin{matrix}CH_2CO\\|\\CH_2CO\end{matrix}\!\!>\!NH + NH_3 + 2H_2O,$$

Ammonium succinate — Succinimide

which is a solid substance having an acidic character, hydrogen of the >NH group being replaceable by metals ; *e.g.*,

$$\begin{matrix}CH_2.CO\\|\\CH_2.CO\end{matrix}\!\!>\!NH + KOH \text{ (alcoholic)} \rightarrow \begin{matrix}CH_2CO\\|\\CH_2.CO\end{matrix}\!\!>\!NK + H_2O$$

Succinimide — Potassium succinimide

(4) When an aqueous solution of the potassium salt of the acid is submitted to electrolysis, it yields ethylene (see page 65).

Tests. (1) When succinic acid is heated in a dry tube, it yields irritating vapour.

(2) A neutral solution of a succinate yields with ferric chloride a flocculent, brownish-red precipitate.

(3) When silver nitrate is added to a neutral solution of succinate, a white precipitate is formed. This, when disolved in just sufficient quantity of dilute ammonia and heated, does *not* undergo reduction (contrast tartaric acid).

7. Polybasic Hydroxy Acids. In their general methods of preparation and chemical behaviour, these compounds resemble the hydroxy monobasic acids already described. The two most important acids of this group are tartaric acid and citric acid.

8. Tartaric Acid. $\begin{matrix}CH(OH)\ COOH\\|\\CH(OH).COOH\end{matrix}$ *Dihydroxy-succinic acid,*

Dihydroxy-butane-diacid. This acid occurs in the form of its potassium hydrogen salt, in grapes and other fruits.

Manufacture. The crude potassium hydrogen tartrate, known as **argol** or **tartar,** is a by-product of the alcohol industry. It is recrystallized from hot water, and the pure product, called cream of tartar, thus obtained is employed for the commercial preparation of tartaric acid.

Cream of tartar is dissolved in water and the solution is neutralized with chalk. Half of the tartaric acid is precipitated as insoluble calcium tartrate, while the other half remains in solution as normal potassium tartrate :—

$$2\begin{vmatrix}CH(OH)COOK\\CH(OH)COOH\end{vmatrix} + CaCO_3 \rightarrow \left[\begin{vmatrix}CH(OH)COO\\CH(OH)COO\end{vmatrix}\right] Ca + \begin{vmatrix}CH(OH)COOK\\CH(OH)COOK\end{vmatrix} + H_2O + CO_2$$

Potassium bitartrate — Calcium tartrate — Potassium tartrate

The precipitate is filtered off, and the filtrate is treated with calcium chloride solution, which precipitates the remaining half of the acid as calcium tartrate :

$$2\begin{vmatrix}CH(OH)COOK\\CH(OH)COOK\end{vmatrix} + CaCl_2 \rightarrow \left[\begin{vmatrix}CH(OH)COO\\CH(OH)COO\end{vmatrix}\right] Ca + 2KCl$$

Calcium tartrate

The calcium tartrate from both the operations is washed with water, and then decomposed with a calculated quantity of dilute sulphuric acid. The precipitated calcium sulphate is filtered off, and the solution is evaporated to obtain crystals of tartaric acid.

Physical Properties. Tartaric acid crystallizes in monoclinic anhydrous prisms. It melts with decomposition at 167° It is readily soluble in water, less so in alcohol, and insoluble in ether.

Reactions. (1) *Acidic Character.* Tartaric acid is a dibasic acid, and, like oxalic acid, forms normal as well as acid salts and esters.

(2) *Reduction.* When heated with hydrogen iodide, it gets reduced to malic acid and finally to succinic acid :

$$\begin{vmatrix}CH(OH).COOH\\CH(OH)\,COOH\end{vmatrix} + 2HI \rightarrow \begin{vmatrix}CH(OH)COOH\\CH_2COOH\end{vmatrix} + H_2O + I_2$$

Tartaric acid — Malic acid (Monohydroxy succinic acid)

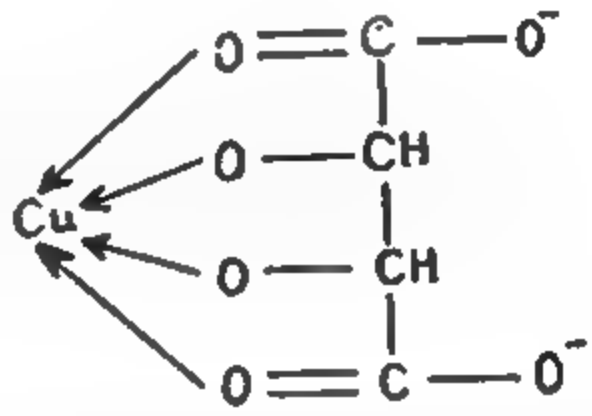
$$\begin{vmatrix}CH.(OH)COOH\\CH_2.COOH\end{vmatrix} + 2HI \rightarrow \begin{vmatrix}CH_2.COOH\\CH_2.COOH\end{vmatrix} + H_2O + I_2$$

Succinic acid

(3) *Reducing Action.* Tartaric acid possesses reducing properties and gives the silver mirror test (*see* Expt. 5).

(4) *Power to Prevent Precipitation of the Hydroxides of Heavy Metals.* Tartaric acid has the property of preventing the precipitation of cupric hydroxide and other heavy-metal hydroxides. The Fehling's solution, the reagent for aldehydes and sugars, is prepared by adding sodium hydroxide to a solution of copper sulphate containing **Rochelle Salt** (sodium potassium tartrate).

The intense blue colour of this solution is due to the complex anion, containing 4—covalent copper, shown in the margin.



Expt. 4. *Preparation of Fehling's Solution.* Mix equal volumes of strong solutions of copper sulphate and Rochelle salt; and then add an excess of sodium hydroxide. A strongly blue-coloured solution (Fehling's solution) will be obtained.

Show the action of Fehling's solution on glucose by warming the two together; a red precipitate of cuprous oxide is produced.

Tests. The more important tests of tartaric acid and its salts are described in the following experiment.

Expt. 5. *Tests of Tartaric Acid.* (1) Heat the acid in a dry tube: immediate charring with the evolution of an odour of burnt sugar.

(2) Heat a little of the acid with concentrated sulphuric acid: rapid charring with evolution of CO, CO_2, SO_2 and an odour of burnt sugar.

(3) Warm the acid (or the precipitate of calcium tartrate from test (5) with a few drops of a solution of resorcinol in concentrated sulphuric acid: add the product to a few c.c's of sodium hydroxide solution; violet red coloration.

(4) Add silver nitrate to a *neutral* solution; white precipitate. Add dilute ammonia, drop by drop, until the precipitate is nearly, but not quite, redissolved, and gently heat the mixture: a silver mirror is formed.

(5) Add calcium chloride to a neutral solution; white crystalline precipitate of calcium tartrate.

Synthesis and Constitution. Tartaric acid can be obtained synthetically from succinic acid. The latter is first converted into dibromo-succinic acid by treatment with bromine and red phosphorus. The dibromo-derivative, when heated with water and silver hydroxide, yields tartaric acid:—

$$\underset{\text{Succinic acid}}{CH_2.COOH \atop | \\ CH_2.COOH} \xrightarrow{\text{Bromination}} \underset{\text{Dibromo-Succinic acid}}{CHBr.COOH \atop | \\ CHBr.COOH} \xrightarrow{AgOH} \underset{\text{Tartaric acid}}{CH(OH).COOH \atop | \\ CH(OH).COOH}$$

The above synthesis of tartaric acid and its conversion into succinic acid by reduction prove that the acid is *dihydroxy succinic acid.*

9. Uses of Tartaric Acid and Tartrates:—

(1) Tartaric acid is used in the preparation of effervescent salines and beverages

(2) The acid potassium tartrate or cream of tartar is used on a very large scale for making baking powders.

(3) **Rochelle** salt or potassium sodium tartrate (got by neutralizing potassium hydrogen tartrate with sodium carbonate is used in the preparation of **Fehling's solution.** This contains copper sulphate Rochelle salt and sodium hydroxide, and is employed in the detection and estimation of glucose and certain other oxidizable organic substances

(4) Tartar emetic or potassium antimonyl tartrate, COOK. CH (OH) CH(OH) COO(SbO); is used as an emetic and as a mordant in dyeing and calico-printing.

10. Citric Acid.

$CH_2.COOH$
|
$C(OH).COOH$, 2 *hydroxy, 1, 2, 3, tri-*
|
$CH_2.COOH$

carboxy-propane.

Occurrence. The acid occurs in the free state in the juice of lemons, limes, *galgals*, oranges, and certain other fruits.

Preparation. (1) Citric acid is prepared on a large scale from the juice of lemons, which contains about 6 to 7 per cent of the acid. The juice is first boiled to coagulate albuminous matter, which is filtered off. The filtrate is neutralized with chalk, and the liquid is boiled. The precipitate of calcium citrate, which separates from the *hot* solution, is washed with hot water, and then decomposed with the calculated quantity of sulphuric acid. Calcium sulphate is filtered off, and the solution is concentrated to obtain crystals of citric acid.

$$\underset{\text{Citric acid}}{2C_6H_8O_7} + 3CaCO_3 \rightarrow \underset{\text{Calcium citrate}}{Ca_3(C_6H_5O_7)_2} + 3H_2O + 3CO_2$$

$$Ca_3(C_6H_5O_7)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2C_6H_8O_7$$

(2) Another method for the large scale production of citric acid consists in fermenting beet-juice and other sugar solutions with the aid of *Citromyces pfefferianus* and *Citromyces glaber*.

Synthesis and Constitution. Citric acid may be synthesized from glycerol by the following series of reactions :

CH_2OH
|
$CH(OH)$
|
CH_2OH
Glycerol

→ (Heat with HCl in glacial acetic acid)

CH_2Cl
|
$CH(OH)$
|
CH_2Cl
Glycerol 1 : 3.dichlorohydrin

→ (Oxidation with chromic acid)

CH_2Cl
|
CO
|
CH_2Cl
Symmetrical dichloroacetone

→ (HCN)

CH_2Cl
|
$C(OH)CN$
|
CH_2Cl
Dichloroacetone cyanohydrin

→ (Boil with dilute HCl)

CH_2Cl
|
$C(OH).COOH$
|
CH_2Cl
Dichloro-acetonic acid[1]

→ (KCN)

CH_2CN
|
$C(OH).COOH$
|
CH_2CN
Dicyanoacetonic acid

→ (Boil with dilute HCl)

CH_2COOH
|
$C(OH).COOH$
|
$CH_2.COOH$
Citric acid

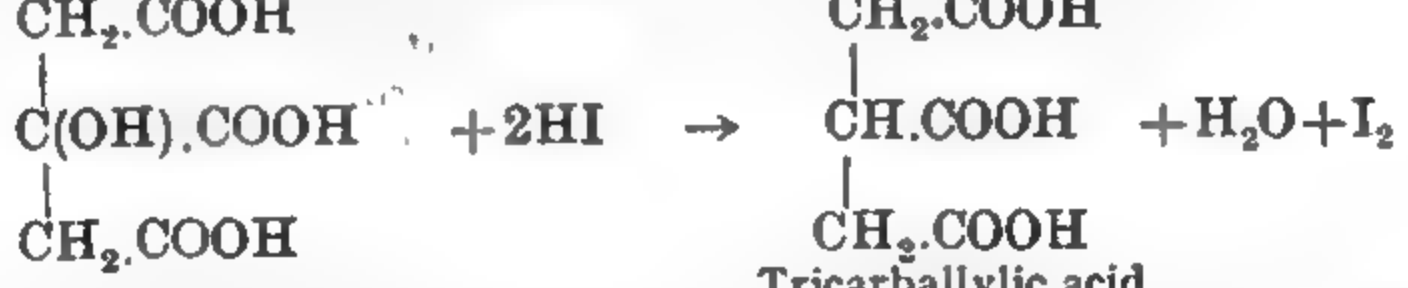
The above synthesis of citric acid shows its constitution, which is further supported by all the reactions of the acid. That it is a monohydroxy tricarboxylic acid is shown by Reactions 3 and 4 given below.

Physical Properties. Citric acid is readily soluble in water and in alcohol but is only sparingly soluble in ether. From the aqueous

[1]The name *acetonic acid* is given to the hydroxy acid obtained from acetone through the cyanohydrin reaction.

solution, the acid crystallizes in large rhombic prisms, which contain 1 molecule of water, and melt at 100°C. The water of crystallization is not lost until the temperature has gone up to 130°. The anhydrous acid melts at 153°.

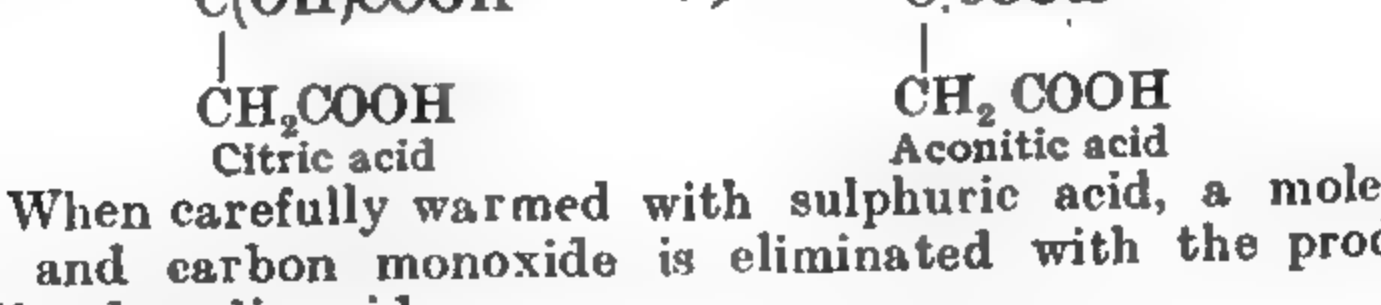
Reactions. (1) Citric acid, being tribasic, forms three series of salts, as for instance, the three potassium salts, all of which are



Mono-potassium citrate | Di-potassium citrate | Tri-potassium citrate

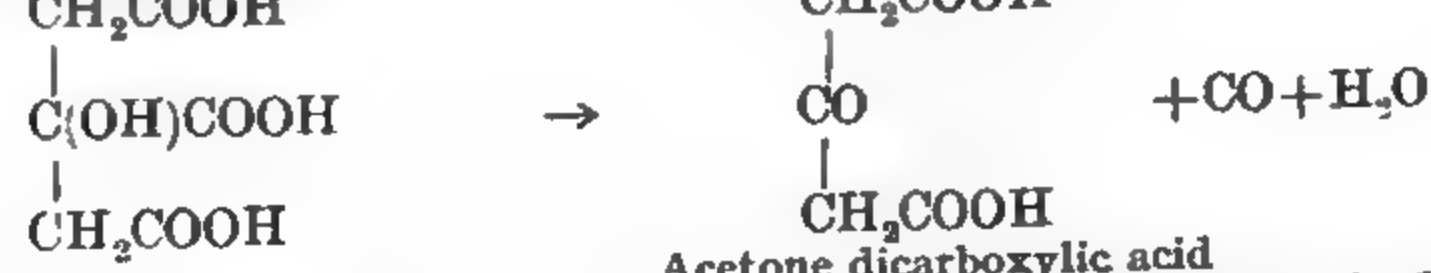
freely soluble in water. Similarly with ethyl alcohol, citric acid forms mono-, di-, and tri-ethyl citrates.

(2) The normal ethyl ester, when treated with acetyl chloride, gives a monacetyl derivative, thus showing that the molecule of citric acid contains one hydroxyl group :



Triethyl citrate | Triethyl aceto-citrate

(3) Like other hydroxy acids, citric acid is reduced by hydrogen iodide, the hydroxyl group being replaced by hydrogen :



Tricarballylic acid

(4) Like tartaric acid, citric acid has the power of preventing precipitation of the hydroxides of certain heavy metals.

(5) *Dehydration.* When heated at 175°, citric acid loses a molecule of water and is converted into an unsaturated acid, called aconitic acid :

Citric acid | Aconitic acid

(6) When carefully warmed with sulphuric acid, a molecule each of water and carbon monoxide is eliminated with the production of acetone dicarboxylic acid :

Acetone dicarboxylic acid

If the heating be continued, the decomposition of the acid proceeds further with evolution of carbon dioxide and *gradual* charring (contrast tartaric acid).

Tests. The more important tests of citric acid and its salts are described below :—

Expt. 6. *Tests of Citric Acid.* (1) When heated in a dry tube, citric acid melts without charring. On continued heating, irritating fumes are evolved, and a *gradual* charring occurs (contrast tartaric acid).

(2) When citric acid or a citrate is warmed with concentrated sulphuric acid, CO is evolved, which, if lighted, burns with a blue flame at the mouth of the tube. After some time, the evolution of CO stops and the flame goes out. The decomposition of the acid now proceeds further with the evolution of CO_2. Finally, a gradual charring of the mass occurs, accompanied by the evolution of SO_2. (Tartrares char almost immediately.)

(3) Calcium chloride, when added to a neutral solution of a citrate, produces no precipitate in the cold. On *boiling* the liquid for some time, a white crystalline precipitate of calcium citrate is formed, since the salt is less soluble in hot than in cold water. This behaviour distinguishes citric acid from tartaric acid.

(4) When silver nitrate is added to a neutral solution of a citrate, a white precipitate of silver citrate is produced. If the precipitate be just dissolved in dilute ammonia and the mixture heated by placing the tube in hot water, no silver mirror is produced (distinction from tartrates.) Continued boiling causes slight reduction.

11. Uses of Citric Acid and Citrates.

(1) Citric acid is used as a mordant in dyeing and calico-printing.

(2) The acid is sometimes used in the preparation of effervescent salines and beverages, for which purpose, however, tartaric acid, being cheaper. is generally substituted.

(3) "*Citrate of Magnesia*", which consists essentially of a mixture of sodium bicarbonate with citric and tartaric acids, together with a little magnesium sulphate, is used in medicines as a laxative.

(4) *Ferric quinine citrate* is used in medicine as a tonic.

(5) *Sodium citrate* is sometimes added to the milk given to babies. It prevents the curdling of milk, and renders it more digestible.

(6) *Ferric Ammonium citrate* is employed in making blue print papers. On one side of a tough, well-sized paper is applied, by means of a camel-hair brush a solution containing ferric ammonium citrate and potassium ferricyanide. and the paper is dried. When an ink drawing on a transparent paper is placed over the sheet prepared as above, and the whole exposed to sunlight, the light, will reduce the ferric salts to the ferrous state, excepting where the ink lines protect it from the action of light. The paper is now washed with water ; the ferrous citrate, produced during the exposure, reacts with potassium ferricyanide, forming the blue-coloured ferrous ferricyanide, which, being insoluble remains fixed within the pores of the paper, while the soluble ferricyanide, is washed out. In this manner, a white pattern on a blue background is obtained.

12. Identification of Oxalic, Tartaric, and Citric Acids. A scheme for the identification of these acids is given in the table on page 198.

Tests of oxalic, tartaric and citric acids:—

Test.	Oxalic acid	Tartaric acid.	Citric acid
1 Heat the solid acid in a dry tube.	Decomposes *without charring*, giving off steam CO, CO_2, and formic acid (characteristic odour).	*Chars at once*, giving off an *odour of burnt sugar*.	Melts without charring; on continued heating, it decomposes and *chars gradually*.
2 Heat with concentrated H_2SO_4.	Dissolves *without charring*, giving CO and CO_2	*Rapid charring* occurs with production of CO, CO_2 and SO_2 also *odour of burnt sugar*.	Dissolves without charring on continued heating, a *gradual charring* occurs.
3 Add $KMnO_4$, to a hot solution acidified with H_2SO_4.	Decolorization of $KMnO_4$ with evolution of CO_2	Same as oxalic acid.	Same as oxalic acid.
4 Add $AgNO_3$, to a *neutral* solution.	*White ppt.*, soluble in dilute ammonia; on warming the ammoniacal solution, *no reduction* occurs.	*White ppt.* If dilute ammonia be added dorp by drop, until the ppt. is nearly, but not quite, redissolved and the mixture gently warmed, a silver mirror is produced.	Same as oxalic acid.
5 Add $CaCl_2$ to a *neutral* solution.	White crystalline ppt., *insoluble* in acetic acid.	White crystalline ppt., produced only on *boiling* the solution.	White crystalline ppt., which, when obtained *fresh* from a *cold* solution, is *soluble* is acetic acid.

QUESTIONS

1. How is oxalic acid prepared on a large scale? What reactions occur between oxalic acid and (*a*) ethyl alcohol, (*b*) sulphuric acid, and (*c*) phosphorus pentachloride? (*Punjab, Inter., 1921*)

2. A dibasic acid containing only carbon, hydrogen and oxygen was found by analysis to contain C, 26·7 per cent; H, 2.2 per cent. A determination of the vapour density of its dimethyl ester gave $\triangle = 59$. What is the acid? (*Manc. Inter., 1910*)
[*Ans.* Oxalic acid, $(COOH)_2$]

3. Describe how a pure sample of oxalic acid, $(COOH)_2 2H_2O$, may be obtained in the laboratory. What tests would you employ to detect the presence of an oxalate? To what different uses are oxalic acid and its salts put?

4. How is oxalic acid made on the large scale? How does it differ in physical and chemical properties from acetic acid? Write equations showing the action of (*a*) heat, (*b*) concentrated sulphuric acid and (*c*) acidified potassium permanganate solution, upon oxalic acid. (*Punjab, Inter, 1942*)

5. Give an account of the preparation of tartaric acid on a commercial scale. How is the presence of this acid detected and how is it distinguished from citric acid? (*Punjab, Inter., 1930*)

6. What are the natural sources of tartaric and citric acids? Give an account of their preparation on a commercial scale and their uses in medicine and commerce. (*Punjab, Inter., 1933*)

7. Indicate a scheme for the preparation of citric acid from the elements carbon and hydrogen. (*Punjab, Inter., 1930*)

8 Give in a tabulat form tests of oxalic, tartaric, and citric acids showing cleraly how the three acids may be distinguished from one another. (*Punjab, Inter., 1931*)

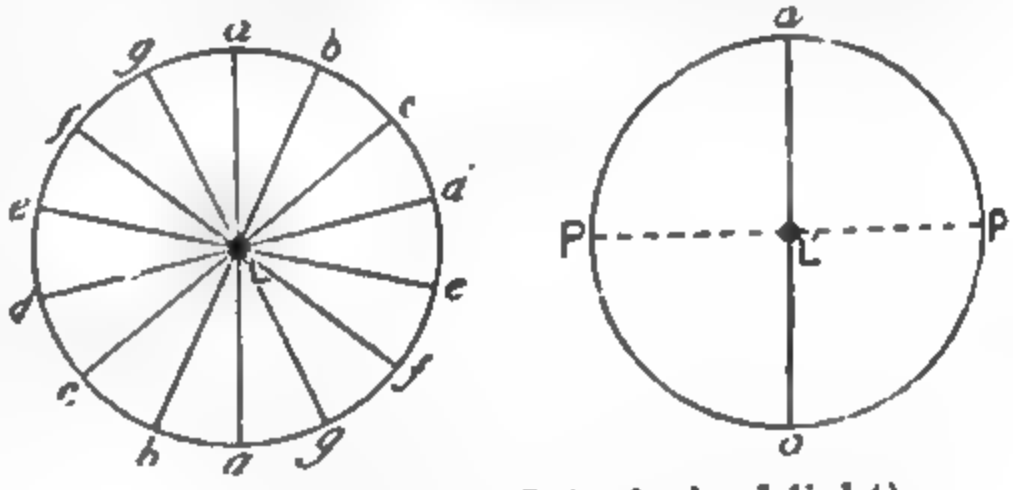
9. Give the preparation and chemical properties of citric acid. (*Bombay, Inter., 1941*)

CHAPTER 21

OPTICAL ACTIVITY AND STEREOISOMERISM

1. Polarization of Light. To understand the phenomenon known as "Polarization", we may take the following illustration: Suppose we have a tightly stretched string knotted near the middle. The knot is free to move in any direction at right angles to the string. Hence, if we pluck the string the knot will be found, in all probability, to describe a series of figures varying between a circle and a straight line. Every point on the string will, of course, be vibrating in a similar manner. Now, suppose that we take a card in which a slit has been cut, slip it on to the string near the knot, and pluck the string once again. This time, the knot will be found to vibrate only in one direction; namely the direction of the slit. Suppose that we now take another piece of card with a slit cut in it, and slip it on to the string near the first card. We shall then see that the knot can vibrate only when the two slits lie parallel to each other: if the slits lie at an angle, the string is gripped, and is not able to vibrate at all at that point.

According to modern theory, a ray of light is propagated through space as vibrations in ether, which take place in all directions perpendicular to the line of propagation of the ray (Fig. 1. *A*). If the ray be passed through a Nicol prism, cut in certain manner from a crystal of Iceland spar (*see* a text book of Physics), the vibrations get restricted and take place only in one direction We say that the light has been *polarized*. In Fig. 1 *A*, a beam, *L*, of ordinary light, is shown to be passing in a direction perpendicular to the plane of the paper, the vibrations in ether taking place in all the directions *aa*, *bb*, *cc*, etc. Fig. 1. *B* shows a beam *L*; of polarized light, in which the vibrations take place only in one direction, *viz*, *aa*. A plane drawn through the direction of the polarized ray, and perpendicular to the direction in which the ether vibrations occur, is called the **plane of polarization**. In Fig. 1 *B* the plane of polarization cuts the plane of the paper along the line *PP*.



A (ordinary light) *B* (polarized light).
Fig. 1.

If the polarized ray be passed through a second Nicol prism, placed with its plane of polarization parallel to that of the first, the ray will pass through it as it did through the first one. If we rotate the second prism, the quantity of the light passing through will continuously diminish, until, when the prism has been rotated through an angle of 90°, the light has been entirely cut off. In other words the position of *maximum brightness*, is followed at an interval of 90° by a position of *maximum darkness*, at an interval of 180° by a second position of maximum brightness, and at an interval of 270° by a second position of maximum darkness. The first Nicol prism, which causes polarization of light, is called the polarizer while the second one, through which the polarized light is examined, is called the **analyser**.

2. Optical Activity. If when the polarizer and the analyser are in the position of maximum darkness, we place between them a tube containing a solution of cane-sugar, the fields of view will be found to have become more or less bright showing that the plane of polarization of light falling on the analyser has been rotated by the cane sugar solution. If now we slowly rotate the analyser towards the right *i.e.*, clockwise, the position of maximum darkness will once again be reached. The angle through which the analyser has to be turned, in order to attain the position of maximum darkness once again, measures the degree of rotation of the plane of polarization by the canesugar solution.

Cane-sugar and other substances that have the power to rotate the plane of polarization in the above manner are said to be **optically active**. If, as in the case of cane-sugar, the analyser is to be turned towards the right (*i e*,, clockwise), to re-attain the position of maximum darkness, the substance is said to be **dextrorotatory** ; if on the other hand, it is to be turned towards the left (anti-clockwise) the substance is called **levorotatory**.

3. Polarimeter. The simple arrangement of two Nicol prisms described above does not give accurate results, for the analyser, when arranged in the position of maximum darkness, can be turned through a small angle in either direction without allowing any light to pass through. Various types of polarimeters have been designed to overcome this difficulty. One of those in common use is the Laurent half shadow polarimeter shown in Fig. 2.

The arrangement of the optical parts of this instrument is shown in Fig. 3. Monochromatic light from a sodium lamp, *S* is passed through a cell, C, containing 6 per cent potassium dichromate solution, which serves to absorb the blue or violet rays. Next it passes through a

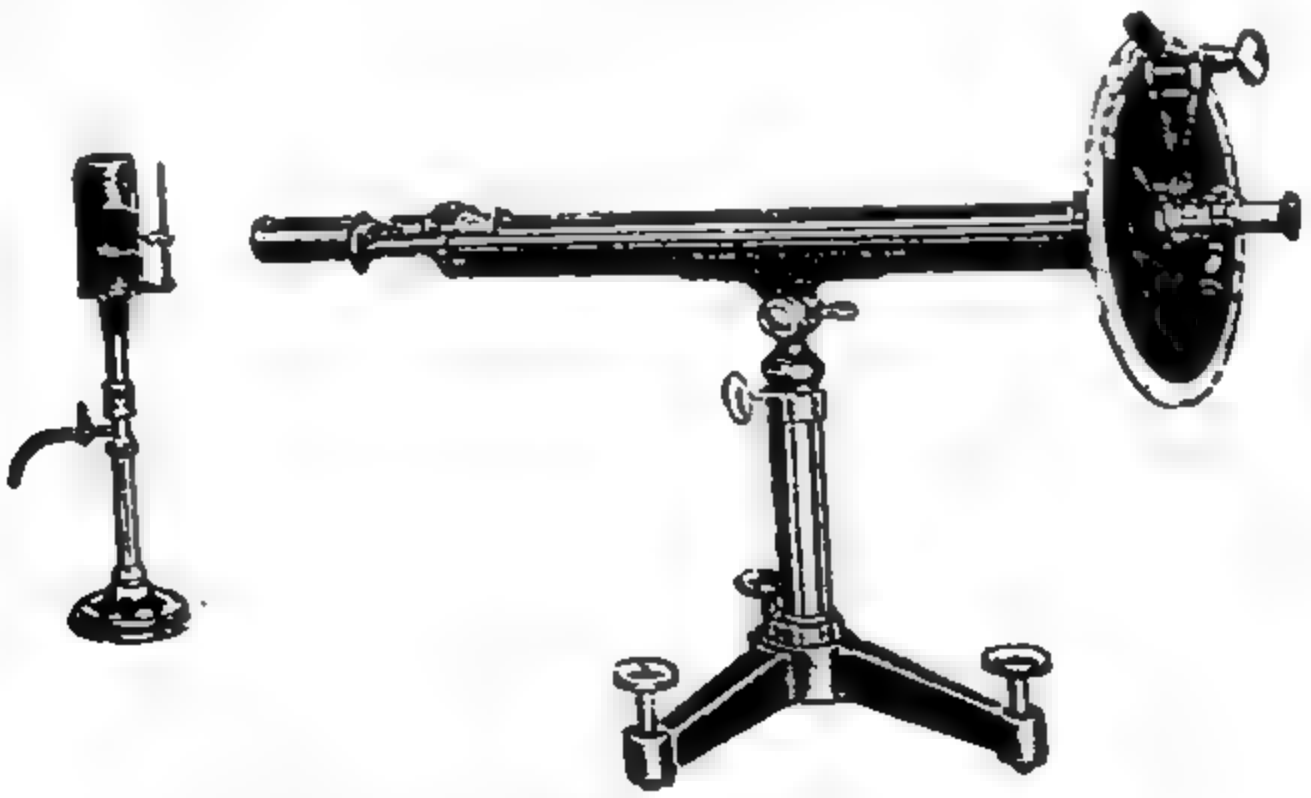


Fig. 2. Laurent's Half-Shadow Polarimeter

collimating lens, *L*, which serves to render the rays parallel, and then through the polarizer, *P*. The polarized light passes through the half shade, *H* (*see* below), and through the liquid under examination contained in the observation tube, *T*. After traversing the liquid, the polarized light passes through the analyser *A*, and finally emerges from the instrument through the eyepiece of the telescope *T'*. The analyser may be

rotated through any desired angle, and the amount of rotation measured on a graduated scale

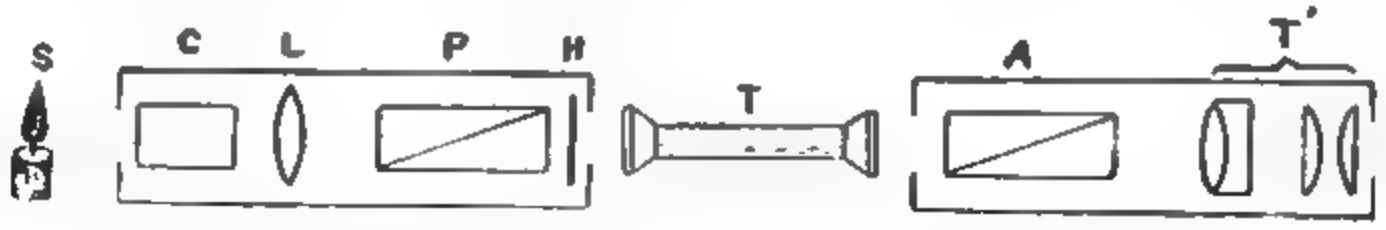


Fig. 3. Optical Parts of the Half-shadow Polarimeter.

The half shade, *H*, serves to determine exactly the point of maximum darkness. It consists of a combination of semicircular plates of glass and quartz. Over a certain range of the scale the right-hand half of the field is darker than the left, beyond this range the left-hand half gets darker than the right-hand half. The intermediate position, where the illumination is uniform on both sides of the field, is taken as the zero point.

Expt. 1. Prepare a 50 per cent solution of pure cane-sugar. (If the solution is not quite clear, it may be clarified by adding a little basic lead acetate solution and filtering through a fluted filter.) Carefully clean an observation tube and the two circular glass discs used to cover the two ends of the tube. Fix up the polarimeter in a dark room, and using an observation-tube filled with distilled water, determine the zero point of the polarimeter. Then replace the observation tube containing water with the one filled with sugar solution, determine the position of equal illumination once again, and read the angle of reaction.

LOUIS PASTEUR

(1822-1895).

a famous French scientist to whom we are indebted for his study of the insomerism of tartaric acids. He is also the well-known discoverer of the treatment for the bite of mad dog.

4. Isomerism of Tartaric Acids. The ordinary tartaric acid, obtained from grape-juice, when examined in the polarimeter is found to be optically active, and turns the plane of polarization of light to the right. The mother liquor obtained in the purification of this acid contains another acid, called **racemic acid**, which, since it possesses exactly the same *chemical* properties as tartaric acid, must have the same structure as the latter. However, racemic acid differs from tartaric acid in its *physical* properties and is optically inactive.

The famous French scientist Pasteur observed in 1846, that the crystals of the **sodium ammonium salt of racemic acid** (which, like the acid itself, is optically *inactive*), when examined under the microscope, could be divided into two distinct sets : In one set certain characteristic facts (*a* and *b*, Fig. 4) were found to be arranged in one particular manner, while in the other the arrangement was related to that of the first set as an object to its mirror image. By a mechanical separation of the two kinds of crystals, he was able to show that one set, when dissolved in water gave a dextro-rotatory solution, while the other set gave a solution which was levorotatory to the same extent The set of crystals showing dextrorotation gave, on treatment with mineral acid, a tartaric acid identical with the natural acid in every respect, while the other set gave a hitherto unknown acid, which in aqueous solution showed *levorotation*. This new acid was, therefore named ***l*-tartaric acid.** On mixing concentrated solutions of equal amounts of the *d*- and the *l*-tartaric acids, a precipitate of optically inactive racemic acid was at once formed.

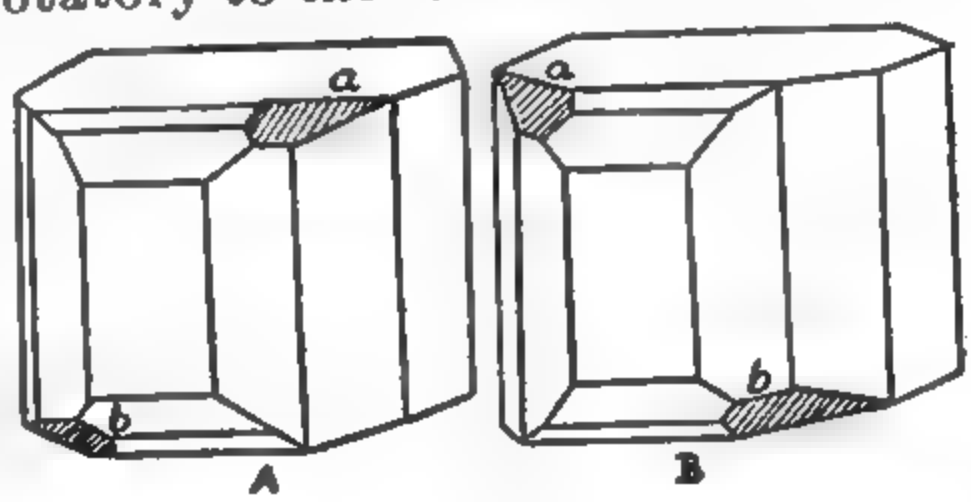


Fig. 4.
Crystals of (A)Sodium Ammonium *d*-Tartrate, (*B*) Sodium Ammonium *l*-Tartrate.

Thus, Pasteur was able to show, both analytically and synthetically, that *racemic acid is a mixture of equal quantities of the d-tartaric acid and the hitherto unknown l-tartaric acid*. For this reason, racemic acid is also called ***dl*-tartaric acid.**

In addition to the above three tartaric acids, a fourth one, known as **meso-tartaric acid,** is also known This is obtained by heating *d*-tartaric acid with water at 105°. Like the racemic acid, the meso-tartaric is optically inactive, but, unlike the former, it *cannot be resolved into optically active components.*

Thus, there are as many as four different forms of tartaric acid, all of which possess exactly the same chemical properties, but differ from one another in certain physical properties, as shown in the table given below :

Acid.	Crystals.	Potassium-hydrogen salt.	Action on plane-polarized light.
1. *d*-Tartaric acid	Monoclinic, anhydrous prisms, m.p. 170°	Sparingly soluble in water	Dextrorotatory
2. *l*-Tartaric acid	Do.	Do	Levo-rotatory.

Acid.	Crystals.	Potassium-hydrogen Salt.	Action on plane-polarized light.
3. Mesotartaric acid	Rectangular, efflorescent plates, containing 1 H_2O and melting at 143°.	Readily soluble in water	Inactive by internal compensation.
4. Racemic acid, or *dl*-Tartaric acid	Rhombic, efflorescent crystals containing 1 H_2O and melting at 206°.	Do	Inactive by external compensation.

5. Le Bel and van't Hoff's Theory. The isomerism of optically active substances, such as the four tartaric acids, is explained by a "space theory" developed independently and almost simultaneously, in 1874, by Le Bel and van't Hoff. According to this theory, *the four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron constructed around the carbon atom as centre.*

By reference to Fig. 5 it can be readily seen that if the four solid angles of the tetrahedron are occupied by the four *different* atoms or groups (*a*, *b*, *c* and *d*), the resulting configuration is capable of existing in a right-handed form and a left-handed form. The mirror-image relationship of the molecule is repeated in the optical and crystallographic properties of the substances. The stereochemical figures such as those given in Fig. 68 are called **space formulae.** By reference to these it will be seen that *the molecule of an optically active compound possesses no plane of symmetry.*

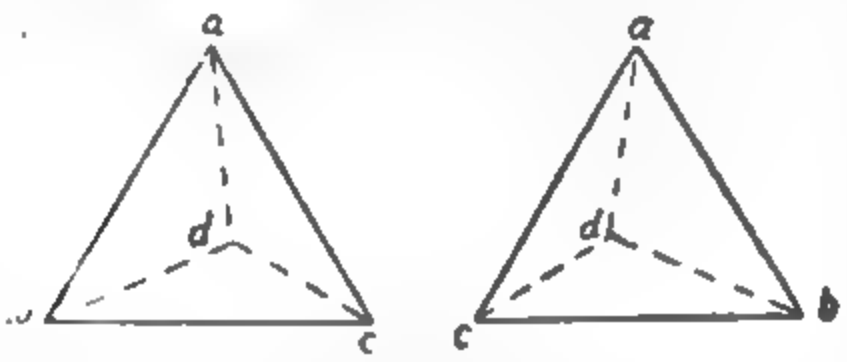


Fig. 5.

A carbon atom linked to four different atoms or groups is known as an **asymmetric carbon atom.** Of course, it is not the atom itself that is asymmetric, but the molecule that contains it. The stereoisomerism exhibited by compounds containing one or more asymmetric carbon atoms is called **optical isomerism,** since it is associated with optical activity, and is to be distinguished from *geometrical isomerism* which is not associated with optical activity.

Le Bel and van't Hoff's theory of stereoisomerism is supported by the following facts :—

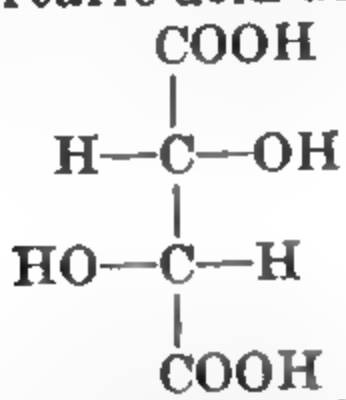
(1) All substances capable of existing in optically active forms possess one or more asymmetric carbon atoms.

(2) If by any means the asymmetric character of the molecule is destroyed, (*e.g.*, in the case of lactic acid, $CH_3.CH(OH).COOH$, by reduction to propionic acid, $CH_3.CH_3.COOH$, the optical activity also disappears.

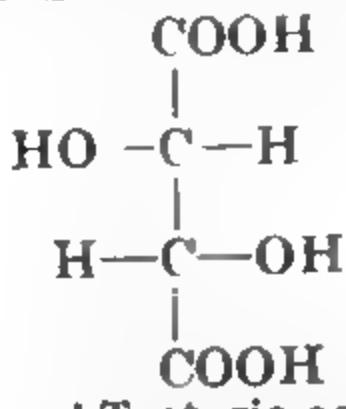
(3) The absence of isomeric forms of such substances as methylene chloride, CH_2Cl_2, which, if all the four carbon valencies lay in the same plane, should exist in two forms :—

In spite of much research, no such isomerism has ever been found to exist.

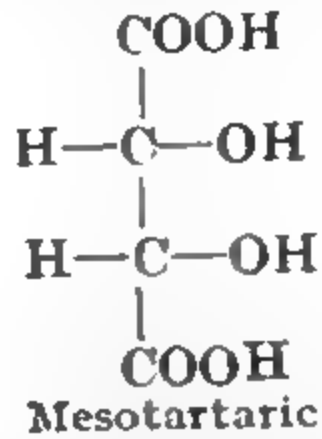
6. Explanation of the Optical Isomerism of Tartaric Acids. The tartaric acid molecule contains two asymmetric carbon atoms. Hence, it is possible to get three different arrangements representing the tartaric acid molecule. In this way, we get three different space formulæ representing the *d*-tartaric acid, the *l*-tartaric acid, and the meso-tartaric acid as shown below :—



d-Tartaric acid



l-Tartaric acid



Mesotartaric acid

In the first case, the two asymmetric carbon atoms have identical configuration[1] ; in the second case, the configurations of the two asymmetric carbon atoms are identical but opposite to those of the first. Hence the effect of the two molecules on plane-polarized light will be equal and opposite. For instance, if the first molecule is dextro-rotatory, the second will be levorotatory to the same extent. In the case of mesotartaric acid, the configuration of the two asymmetric carbon

JACOBUS HENRICUS VAN'T HOFF (1852—1911)

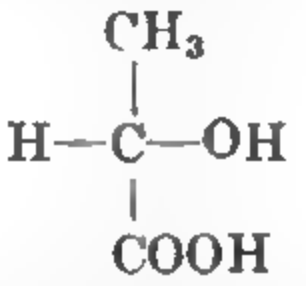
a Dutch physical chemist, who, in 1874, put forward the "Theory of Asymmetric Carbon Atom", which forms the basis of Stereochemistry.

[1]This can be best shown by means of carbon models.

atoms are opposite to one another, so that if one of them is dextro-rotatory, the other will be levo-rotatory to the same extent. Hence the molecule as a whole will be optically inactive, due to what is termed **internal compensation**. The fourth isomer, *i.e.* racemic acid, when in aqueous solution, is a mixture of equal quantities of *d*-and *l*-acids. Hence, the dextro-effect of the *d*-molecuels is exactly counterbalanced by the levo-effect of the *l*-molecules, and the substance is inactive by **external compensation**.

7. **Optical Isomerism of Lactic Acids.** In addition to the common lactic acid obtained from sour milk (Sec. 5, *chap.* 18), which is optically inactive, there exists a *dextrorotatory* lactic acid. This is present in meat juice, and is called **sarcolactic acid** (Gk. *sarkos*, flesh).

The lactic acid molecule—



contains an *asymmetric carbon atom, viz.*, the one printed in bold type. The acid should, therefore, exist in three different forms, namely the *d*-form, the *l*-form and the racemic mixture of the two forms, which, consisting as it does equal quantities of *d*-and *l*-forms, should be optically inactive. Ordinary lactic acid, obtained by the lactic fermentation of sugars and by synthetic methods, is the optically inactive recemic mixture. By the fractional crystallization of the strychnine salt of this acid, it can be resolved into the *d*- and *l*-lactic acids. The following table summarizes the distinctive physical properties of the three acids :—

Property	*d*-Lactic acid	*l*-Lactic acid	*dl*-Lacic acid
1. Action on polarized light	Dextro-rotatory	Levo-rotatory.	Inactive.
2. Melting point.	26°	26°	18°
3. Zinc salt.	Crystallizes with $2H_2O$, and is readily soluble in water.	Similar to *d*-lactate	Crystallizes with $3H_2O$ and is sparingly soluble in water.

QUESTIONS

1. Explain the following terms ; (*a*) *polarized light*, (*b*) *optical activity*, (*c*) *optical isomerism*, (*d*) *asymmetric carbon atom.*
2. Discuss the optical isomerism of tartaric acids.
3. How many lactic acids are known ? What reason have you to believe that they all possess the same structural formula ? How is the existence of isomerism explained ?

CHAPTER 22

CARBOHYDRATES

1. Carbohydrates. The Carbohydrates constitute a group of organic substances, which are of the greatest importance from the theoretical as well as the practical point of view. With but a few exceptions, the members of this group may be represented by the general formula $C_x(H_2O)y$, hence the name "carbohydrates" (*i.e.*, compounds of carbon with water). The term has, however, lost its original significance, because the molecular formulæ of some of the members of this group (*e.g.*, rhamnose and fucose, $C_6H_{12}O_5$) do not agree with the above formula. On the other hand, a number of organic compounds (such as formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$), whose formulæ agree with the above general formula, are entirely different from the carbohydrates in chemical behaviour.

The carbohydrates are divided into three main classes according to their molecular complexity :

(1) **Monosaccharides** (also known as *monosachoroses* or *monoses*). Glucose fructose, each of which possesses the molecular formula $C_6H_{12}O_6$, belong to this group.

(2) **Disaccharides** (also known as *disaccharoses* or *dioses*). The most familiar example of this class is cane-sugar, $C_{12}H_{22}O_{11}$.

(3) **Polysaccharides** (also called *polysaccharoses* or *polyoses*, $(C_6H_{10}O_5)n$. Starch, cellulose and other complex carbohydrates belong to this class.

The members of the first two groups, collectively known as **sugars**, are crystalline, soluble solids with a sweet taste, while those of the third group, called **non-sugars**, are amorphous, insoluble aud tasteless.

2. Glucose, *Dextrose, Grape sugar*, $C_6H_{12}O_6$. This is the most important monosaccharide.

Occurence. Glucose occurs, together with another monosaccharide called *fructose* or fruit sugar, in grapes mangoes and other sweet fruits, and also in honey and nectar of certain flowers. The urine of patients suffering from diabetes may contain as much as 10 per cent of this sugar.

Preparations. (1) *From Cane-Sugar.* Glucose can be readily prepared in the laboratory by hydrolysing cane-sugar with hydrochloric acid :—

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The cane-sugar is dissolved in rectified spirit, a small proportion (about 5 per cent) of concentrated hydrochloric acid is added, and the mixture heated at 50° for about 2 hours. On allowing the reaction product to cool, glucose, being much less soluble in alcohol than fructose, crystallizes out.

(2) *From Starch.* On a commercial scale, glucose is prepared by the hydrolysis of starch :—

$$\underset{\text{Starch}}{(C_6H_{10}O_5)x} + xH_2O \rightarrow \underset{\text{Glucose}}{xC_6H_{12}O_6}$$

Starch, made into a thin paste with hot water, is boiled under pressure

with a small quantity of dilute sulphruic acid, until a few drops of the liquid give no coloration with a drop of iodine solution. The acid is then neutralized with chalk, and the liquid is filtered. The filtrate is decolorized with animal charcoal, and evaporated in vacuum pans to syrup, which on being allowed to cool sets to a solid mass of crystals.

Uses. Glucose is used as a substitute for cane-sugar by bakers and confectioners. It is also used in the fruit preservation and wine industries. Very large quatities of corn syrup or glucose syrup are manufactured in the United States from maize starch by hydrolysis.

Physical Properties. Glucose is a colourless, crystalline substance, much less sweet than cane-sugar. It is readily soluble in water, from which it separates as crystals containing one molecule of water and melting at 80°. It is sparingly soluble in alcohol, from which it crystallizes as anhydrous needles, melting at 146°. Glucose is *dextrorotatory*, *i.e.*, its solutions turn the plane of polarized light towards the right. Hence, it is also called *d*-glucose.

Chemical Properties. Glucose has been shown to possess the structural formula

$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CHO \end{array}$$

Hence it possesses the properties of a polyhydroxy aldehyde. A sugar such as glucose, that contains an aldehyde group in its molecule is called an **aldose**.

The following are the chief chemical properties of glucose :

(1) *Acetylation.* When heated with acetic anhydride and a little zinc chloride, glucose gives a **pentacetyl derivative** :

$$\begin{array}{l} CH_3COO.CH_2 \\ | \\ (CH_3COO.CH)_4 \\ | \\ CHO \end{array}$$

This proves that the glucose molecule contains *five* hydroxyl groups.

(2) *Reductions.* When reduced by means of sodium amalgam in aqueous solution, glucose gives the corresponding primary alcohol, called **sorbitol** (compare acetaldehyde, which gives ethyl alcohol) :—

$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CHO \end{array} + 2H \rightarrow \begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Glucose (an aldehyde) — Sorbitol (a primary alcohol)

(3) *Reducing Action.* Glucose, like other aldehydes, possesses reducing properties, being readily oxidized to the corresponding mono- and dicarboxylic acids, called gluconic acid and saccharic acid respectivly.

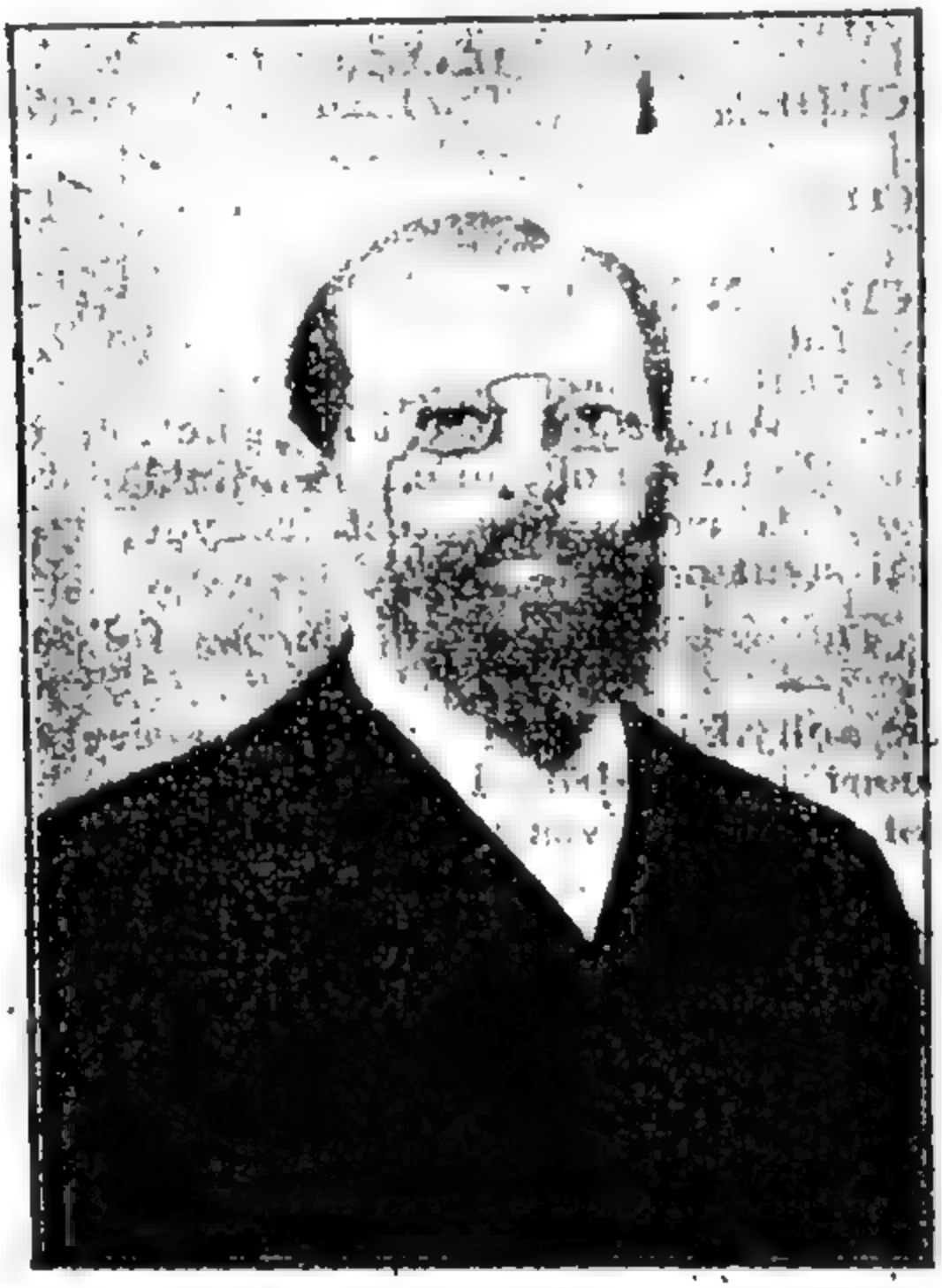
$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} \xrightarrow{+O} \underset{\text{Gluconic acid}}{CH_2OH.(CHOH)_4.COOH}$$

$$\xrightarrow{+O} \underset{\text{Saccharic acid}}{COOH.(CHOH)_4.COOH}$$

For this reason, glucose gives the **silver mirror test** and also reduces the **Fehling solution** (compare other aldehydes).

(4) *Addition of Hydrogen Cyanide.* Glucose, like other aldehydes, combines with a molecule of hydrogen cyanide, yielding a *cyanohydrin* :

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} + HCN \rightarrow \underset{\text{Glucose cyanohydrin}}{CH_2OH.(CHOH)_4CH(OH)CN}$$



EMIL FISCHER (1852-1919)

a brilliant German chemist, who is well-known for his researches on sugars and also on certain other branches of Organic Chemistry.

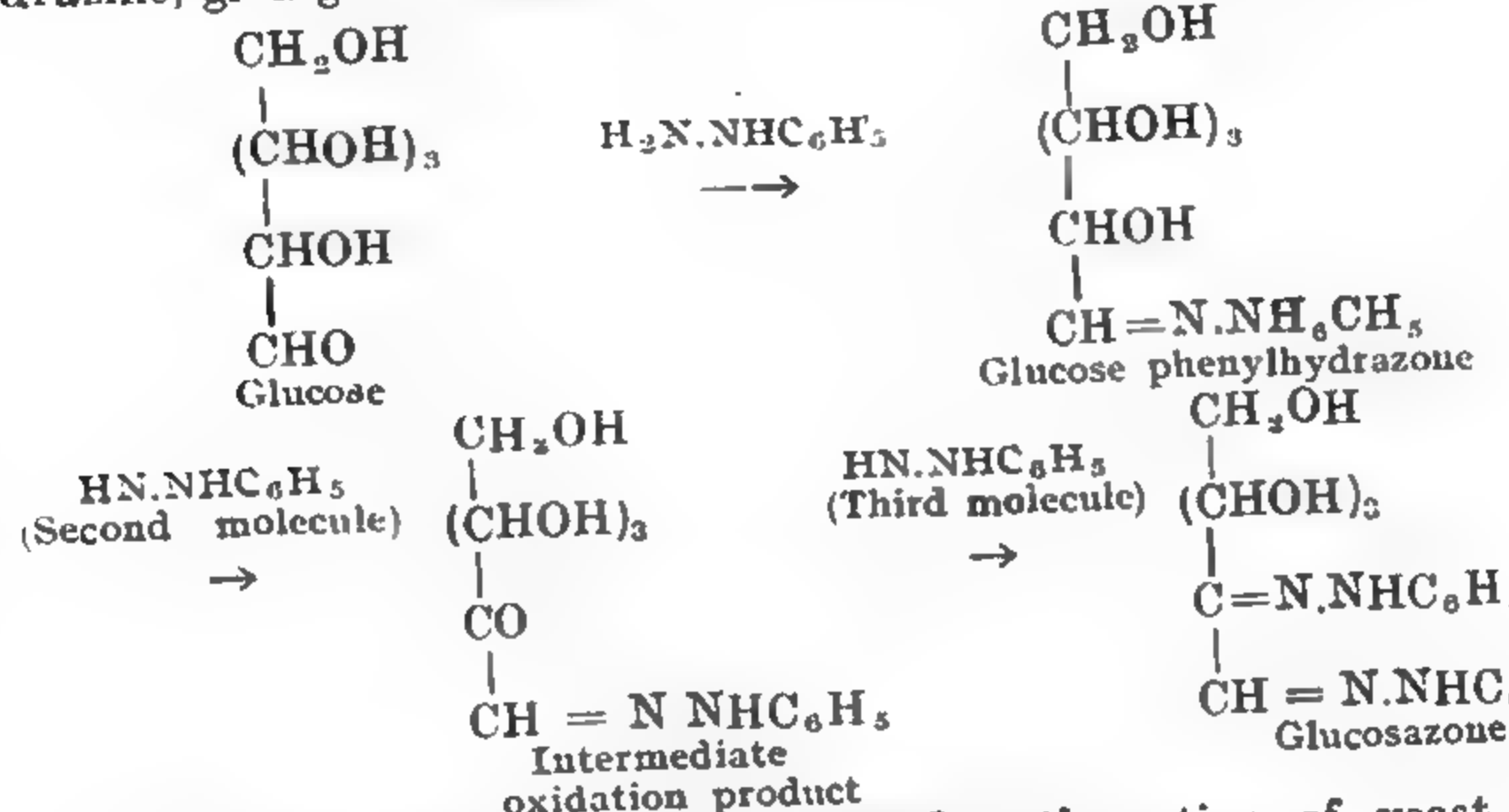
(5) *Reaction with Hydroxylamine.* When treated with hydroxylamine, glucose gives an *oxime.*

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} + H_2NOH \rightarrow$$

$$CH_2OH.(CHOH)_4.CH{=}NOH + H_2O$$
Glucose oxime

(6) *Reaction with Phenylhydrazine.* Glucose, like other aldehydes, reacts with phenylhydrazine in the cold to give a *phenylhydrazone.* When heated with an excess of phenylhydrazine, the phenylhydrazone first formed is oxidized by a second molecule of phenylhydrazine (which is itself reduced to ammonia and aniline) with the production of a

new > CO group, which then reacts with a third molecule of phenylhydrazine, giving an **osazone :**



(7) *Fermentation.* When subjected to the action of yeast, glucose gets decomposed into ethyl alcohol and carbon dioxide.

(8) *Resinification.* Glusose, like acetaldehyde, resinifies on being heated with an alkali solution.

Constitution. The constitution of glucose follows from the following considerations :—

(1) With acetic anhydride it gives a pentacetyl derivative ; hence the molecule must contain 5 hydroxyl groups.

(2) On oxidation, glucose gives acids (gluconic and saccharic) containing the *same* number of carbon atoms as the sugar itself. This suggests the presence of an aldehyde group and a primary alcohol group in the molecule.

(3) On treatment with hydrogen cyanide, followed by hydrolysis and reduction, glucose gives *normal* heptylic acid, which is known to contain a straight chain of 7 carbon atoms, with a terminal COOH group, $CH_3 \cdot (CH_2)_5 \cdot COOH$. Hence it appears that glucose is a straight chain compound having a terminal — CHO group.

The above reaction are explained by the aldohexose formula,

$$\begin{array}{l} CH_2OH \\ | \\ \text{usually } (CHOH)_4 \\ | \\ CHO \end{array}$$

assigned to glucose.

Expt. 1. *Test of Glucose:—*

(1) *Moore's Test.* Boil a solution of glucose with sodium hydroxide : Notice that it turns yellow, then dark brown, and gives out a smell of caramel.

(2) *Silver-mirror Test.* Repeat Expt. 1 p. 117, using a solution of glucose instead of acetaldehyde. Notice the formation of a silver mirror.

(3) *Reduction of Fehling's Solution.* Repeat Expt. 42, p. 145, using glucose instead of acetaldehyde. Notice the formation of a red precipitate of cuprous oxide.

3. Fructose, *Fruit Sugar. Levulose,* $C_6H_{12}O_6$.

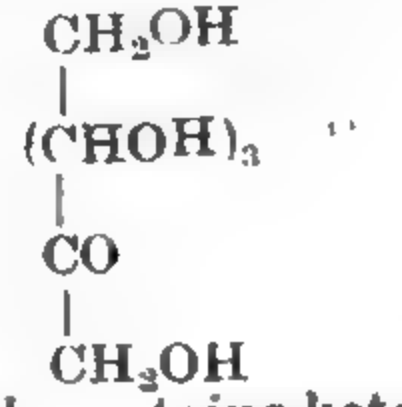
Occurrence. This sugar occurs, together with glucose, in honey, nectar, and the juice of sweet fruits.

Formation. As already mentioned, the hydrolysis of cane-sugar yields an equimolecular mixture of glucose and fructose, from which, however, it is difficult to isolate pure fructose.

Manufacture. Fructose is commercially prepared by the hydrolysis of inulin, a starch obtained from *dahlia* tubers and Jerusalem artichokes. The method is similar to that employed for the manufacture of glucose from ordinary starch.

Physical Properties. Fructose forms anhydrous, sweet crystals melting at 95°, and is readily soluble in water. Its solutions are *levorotatory* (hence the name levulose).

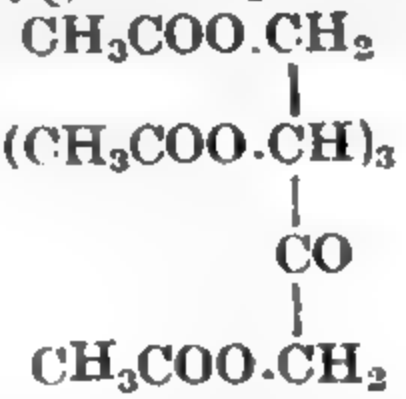
Chemical Properties. Fructose has been shown to possess the structural formula :



A sugar, such as fructose, which contains keto group in its molecule is termed a **ketose.**

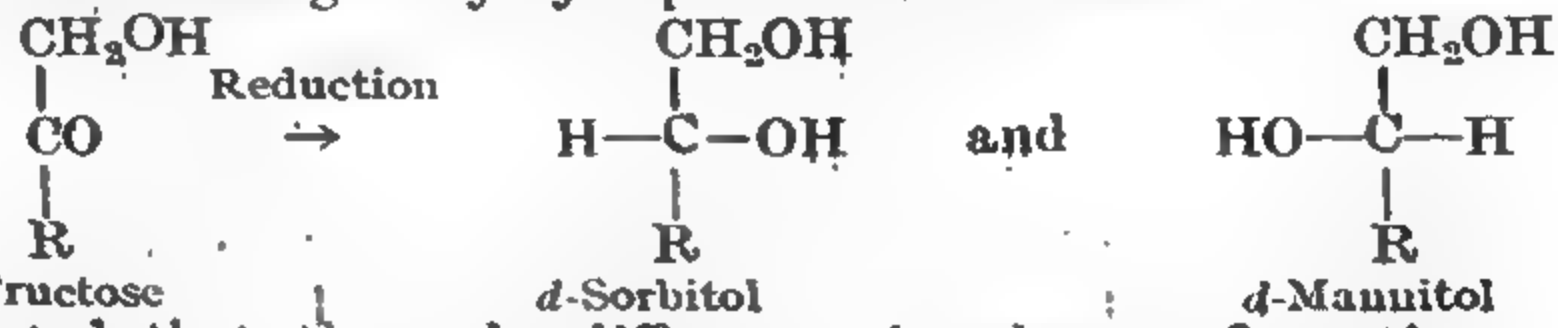
In most of its chemical properties, fructose closely **resembles** glucose. Its chief reactions are :—

(1) *Acetylation.* When heated with acetic anhydride and a little zinc chloride, fructose, like glucose, gives a **pentacetyl derivative** :—



This proves that the fructose molecule contains *five* hydroxyl groups.

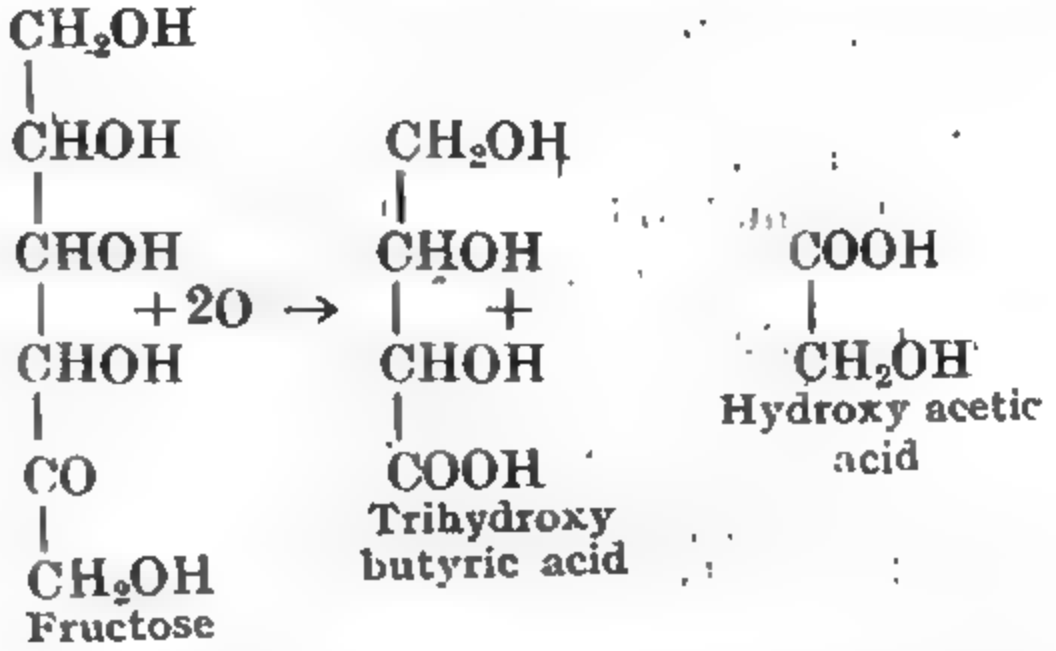
(2) *Reduction* When reduced by means of sodium amalgam in aqueous solution, fructose gives a mixture of **sorbitol and mannitol** (contrast glucose which gives only sorbitol). Both sorbitol and mannitol are primary alcohols possessing the same structure but different configurations. Representing the $CH_2OH(CHOH)_3$—part of the molecule of fructose by *R*. the change may by represented as follows :



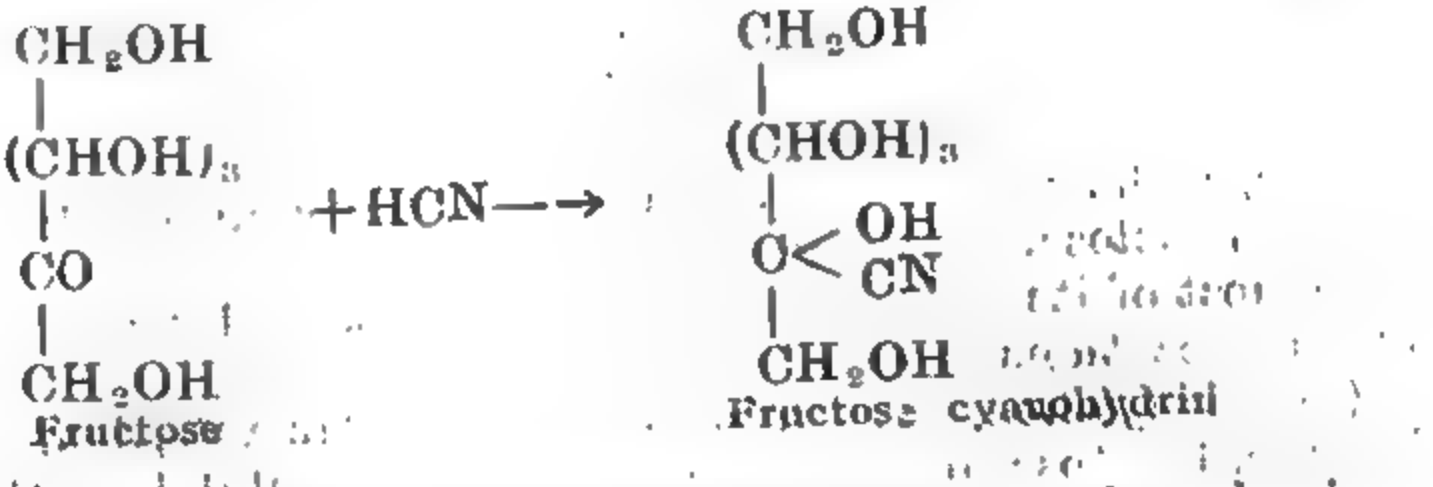
It should be noted that the only difference in the configuration of sorbitol and that of mannitol lies in the newly produced asymmetric carbon atom printed in the bold type.

(3) *Reducing Action.* Fructose, like glucose, possesses active reducing properties, and gives the silver-mirror test and reduces the Fehling solution. In this respect, it differs from simple ketones such as acetone. During these reactions, the molecule breaks up (compare keto-

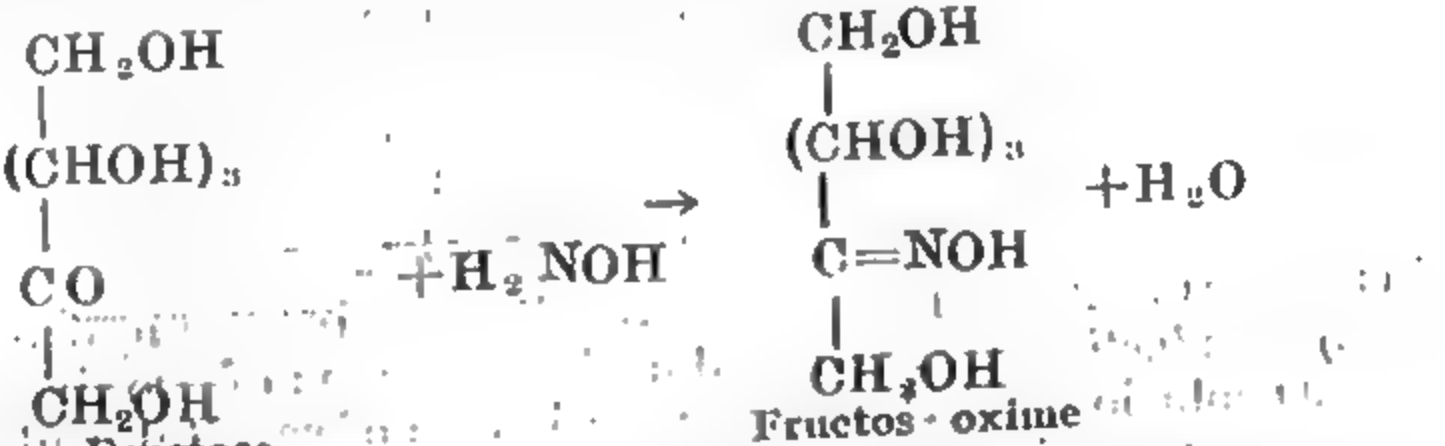
nes), a mixture of **hydroxyacetic acid** and **trihydroxybutyric acid** being produced :—



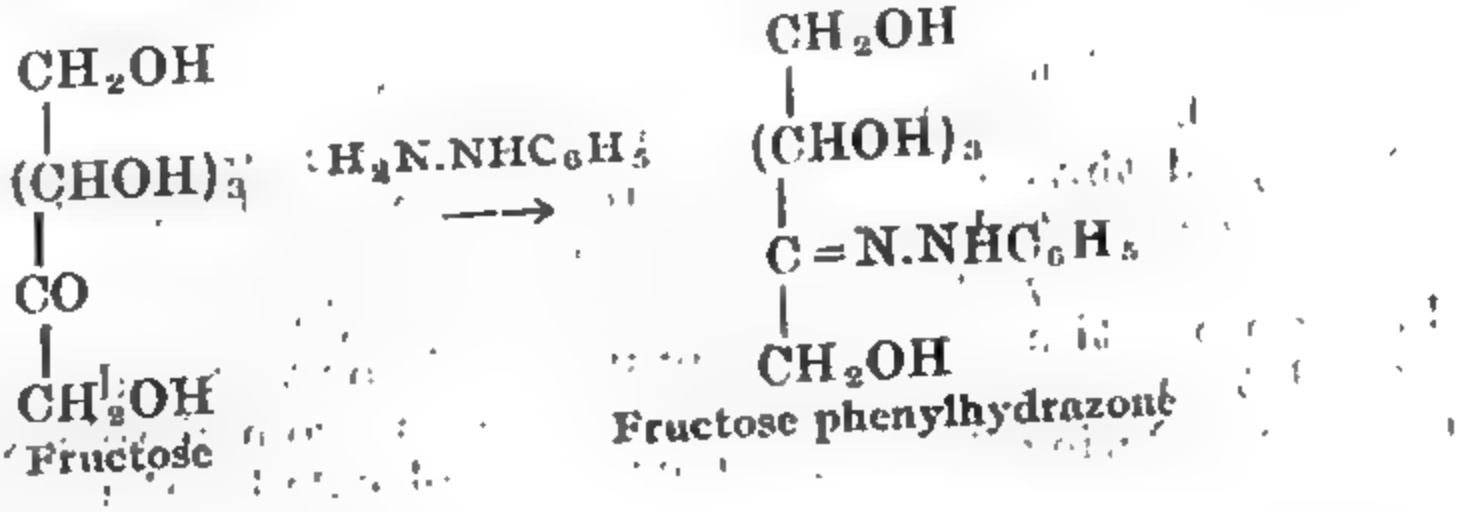
(4) *Addition of Hydrogen Cyanide.* Fructose, like other ketones, combines with a molecule of hydrogen cyanide, yielding **fructose cyanohydrin** :—

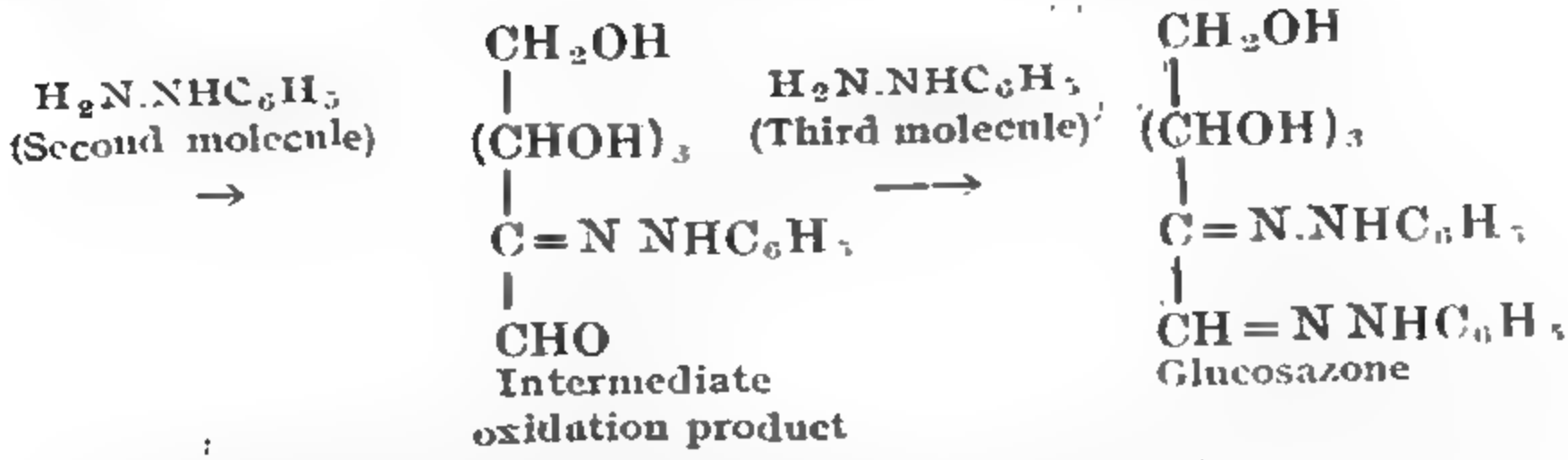


(5) *Reaction with Hydroxylamine.* When treated with hydroxylamine fructose gives fructose oxime :—



(6) *Reaction with Phenylhydrazine.* Fructose, like other ketones, reacts with phenylhydrazine in the cold to give **fructose phenylhydrazone** When heated with an excess of phenylhydrazine, the phenylhydrazone, first formed, is oxidized by a second molecule of phenylhydrazine, as in the case of glucose, with the production of a — CHO group. The latter then reacts with a third molecule of phenylhydrazine, giving glucosazone :—





The fact that fructose and glucose give the *same* osazone proves the **configurational relation hip** of the two sugars.

(7) *Fermentation.* Fructose, like glucose, is fermentable by yeast, giving the same products as glucose.

Tests. Fructose may be identified by the tests described in the following experiment.

Expt. 2. *Tests of Fructose :—*

(1) *Silver-mirror Test.* See **Expt.** 1, p. 210.

(2) *Reducing of Fehling's solution.* See **Expt.** 1, p. 210.

(3) *Action of concentrated Hydrochloric Acid.* Boil a solution of fructose with concentrated hydrochloric acid. Note that the solution becomes at first red or red-brown, and ultimately turns dark brown.

(4) *Selivanoff's Test.* Dilute some concentrated hydrochloric acid with an equal volume of water. Add a few crystals of resorcinol and a few drops of fructose solution, and heat. The solution will turn red in colour, and a brownish-red precipitate will be deposited. Add alcohol ; the precipitate dissolves to give a red solution.

Use. Fructose has a sufficiently sweet taste to be used as a substitute for cane-sugar by patients suffering from diabetes.

4. Distinction between Glucose and Fructose. Glucose and fructose differ from each other in the following respects : –

(1) Glucose is dextro-rotatory, while fructose is levo-rotatory.

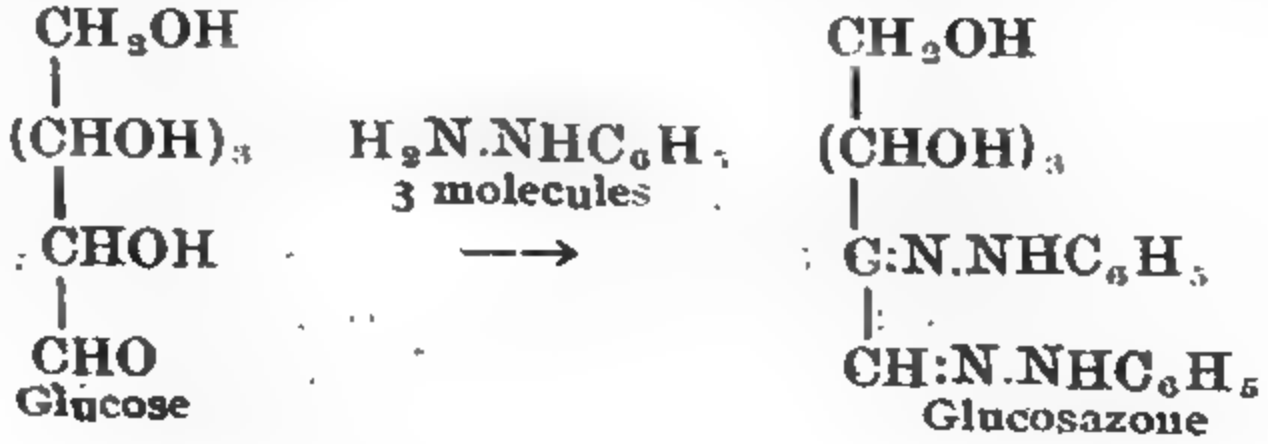
(2) On reduction, glucose gives sorbitol while fructose gives a mixture of sorbitol and mannitol.

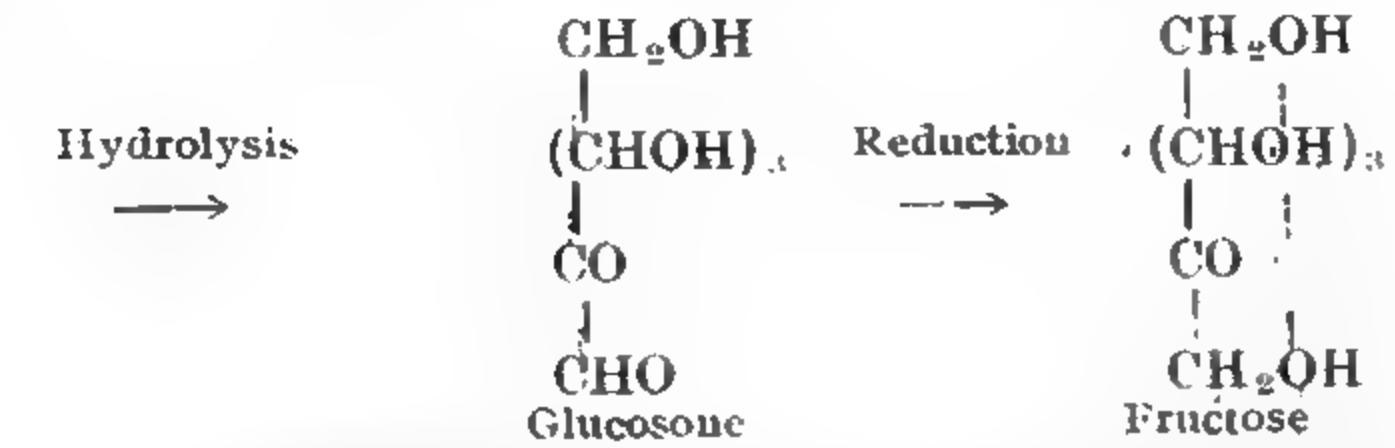
(3) When subjected to oxidation, glucose gives acids (gluconic and saccharic) containing the same number of carbon atoms as the sugar itself. Fructose, on the other hand, undergoes oxidative breakdown, yielding a mixture of acids (hydroxyacetic and trihydroxybutyric) containing a smaller number of carbon atoms than the sugar.

(4) With resorcinol and hydrochloric acid, fructose gives a deep-red coloration and ultimately an alcohol-soluble brown red dye.

(5) Glucose gives Moore's test with sodium hydroxide.

5. Conversion of Glucose into Fructose. To obtain fructose from glucose, the latter is first converted into glucosazone (*p.* 168), which on hydrolysis, yields glucosazone. This last compound upon reduction passes into fructose.





Glucosone Fructose

6. Glucosides. Glucosides are derivatives of the ether type formed by the combination of a monosaccharide (commonly glucose) with one or more other substances. The simplest compounds of this class have been synthesized by Emil Fischer by allowing a monosaccharide to react with an alcohol in the presence of hydrogen chloride : *e.g.*,

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + CH_3OH \rightarrow \underset{\text{Methyl glucoside}}{C_6H_{11}O_5OCH_3} + H_2O$$

These compounds do *not* combine with hydrogen cyanide, hydroxyl-amine or phenylhydrazine. Hence, they contain no >CO group. When heated with dilute acids, they are hydrolysed to re-form the monosaccharide and the alcohol. Hence, we conclude that it is at the keto group that the combination of the sugar with the alcohol molecule has occurred.

The study of these simple glucosides has been very helpful in establishing the constitution of sugars. It led Fischer to the conclusion that the polysaccharides are analogous to glucosides ; they are the glucosides of the monosaccharides themselves.

More complex glucosides are found very widely distributed in the vegetable kingdom. A typical example is **amygdalin** $C_{20}H_{27}NO_{11}$, which is present in bitter almonds It crystallises in colourless prisms melting at 208°C, and is readily soluble in water. Amygdalin is decomposed by the hydrolytic action of the enzyme **emulsin,** also present in bitter almonds, to give glucose, benzaldehyde and hydrogen cyanide :—

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O \rightarrow \underset{\text{Glucose}}{2C_6H_{12}O_6} + \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Hydrogen cyanide}}{HCN}$$

Salicin, present in Salix and willow bark and various *tannins* which occur in oak bark, acacia bark, tea leaves etc., are other examples of glucosides.

7. Sucrose, Cane Sugar, *Saccharose*, $C_{12}H_{22}O_{11}$.

Occurrence. Cane-sugar, which is the most important of all sugars, occurs in the juice of certain plants notably the sugar-cane and sugar-beet.

Manufacture. The two most important sources of commercial cane-sugar are : (1) the sugar-cane (Fig. 1), and (2) the sugar-beet (Fig. 2).

(1) **From Sugar-cane.** The manufacture of cane-sugar from sugar-cane consists of three distinct steps :—

(*i*) *Extraction of the Juice.* For this purpose, the canes are crushed in a cane-mill or a hydraulic press.

(*ii*) *Purification of the Juice* The juice contains, in addition to sugar and water, small quantities of vegetable proteins, pectic substances (colloidal carbohydrates) and mineral salts. It must be "defecated" immediately after extraction ; if allowed to stand, the pectic substances

undergo fermentation, producing peotic acids, which catalyse the conversion of cane-sugar into noncrystallizable invert sugar.

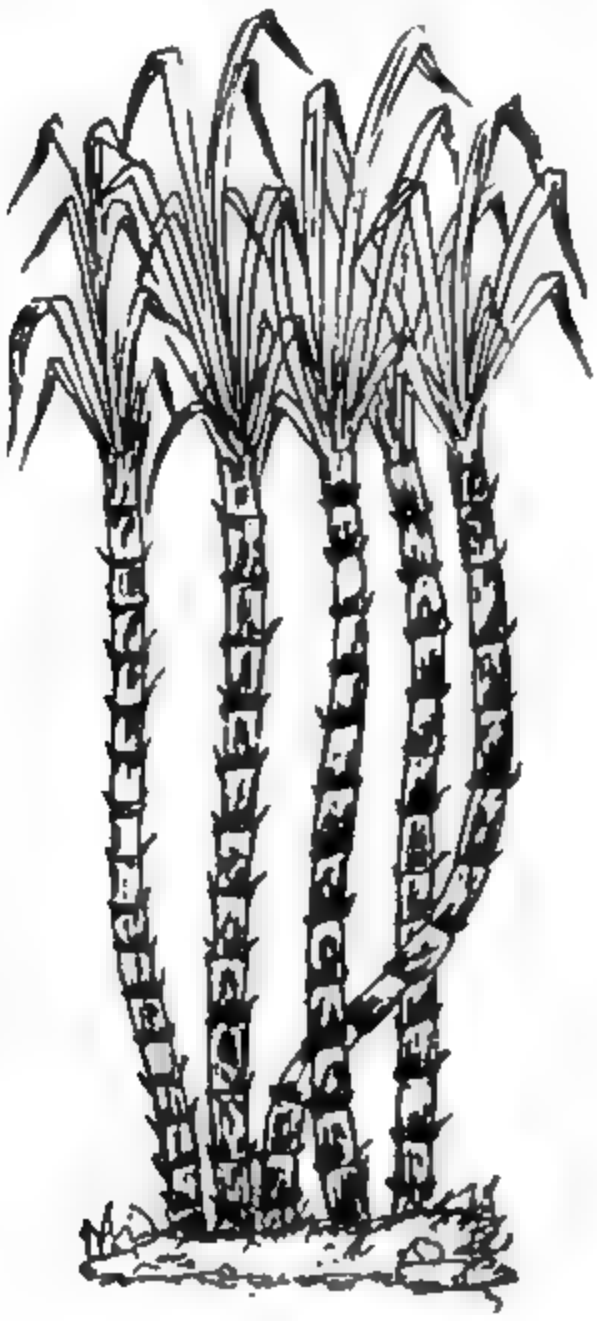


Fig. 1. Sugar-cane.

Fig. 2. Sugar-beet.

The juice is, therefore, at once run into defecator tanks heated by steam coils, and treated with 2 or 3 per cent of lime **(defecation)**. By this treatment, the proteins are coagulated and the pectic substances are precipitated as insoluble pectates of calcium. These rise to the surface, forming a thick scum which is removed. The excess of lime is thrown down as calcium carbonate by blowing in carbon dioxide **(carbonation)**, and the liquid is then filtered. Instead of carbon dioxide, sulphur dioxide is frequently used **(sulpoitation)**, and yields a liquid of much better colour.

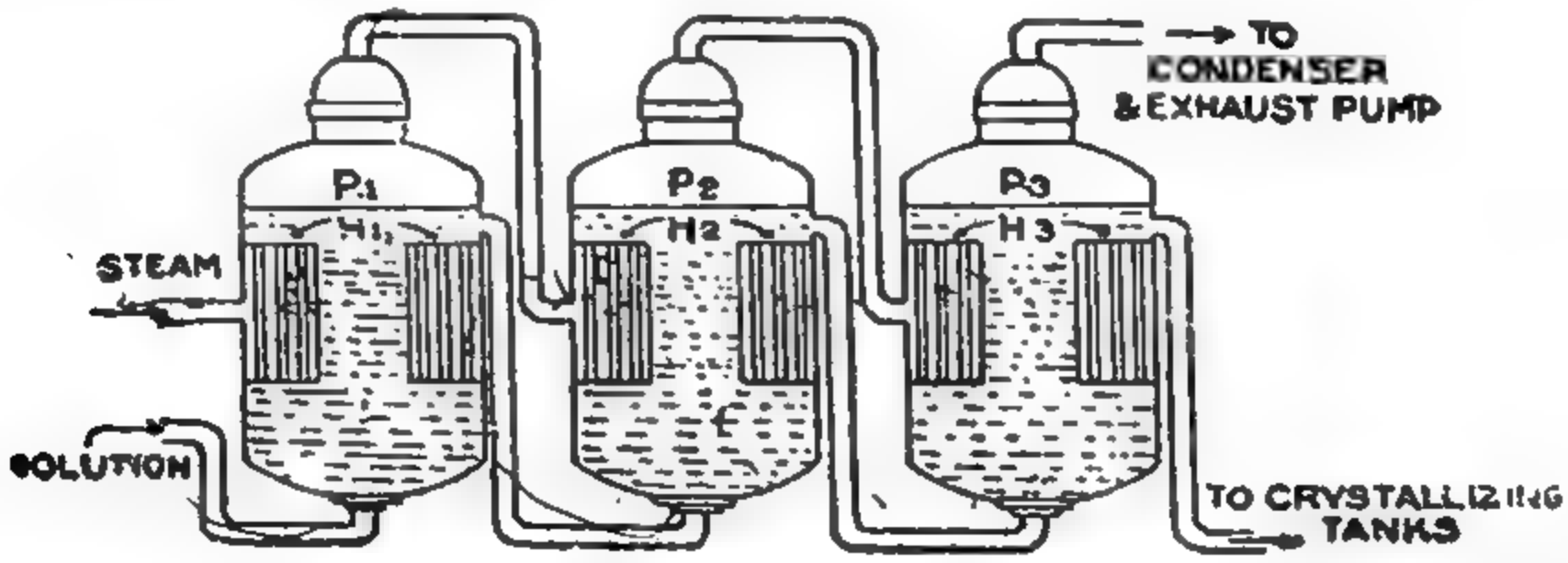


Fig. 3. Multiple- effect evaporator (diagrammatic).

(iii) *Concentration and Crystallization.* The clarified juice is evapo-

rated to a syrup under reduced pressure in "multiple effect" vacuum pans[1] (Fig 3). Carbon dioxide is once again passed through the syrupy liquid to decompose any calcium saccharate still present in solution. The precipitated calcium carbonate is filtered off, and the syrup further evaporated *invacuo* to the crystallization point. The liquid is then run out from the pans and cooled The crystals are separated from the syrupy mother liquor, known as "molasses," by means of centrifugal machines.

(2) ***From Beet-root*** Beet-root contains about 15 per cent of sugar, which it is not possible to recover by simple pressing. The process employed is known as the diffusion process This is really a process of dialysis, which allows a free passage of sugar, but not of albuminous and other colloidal matter.

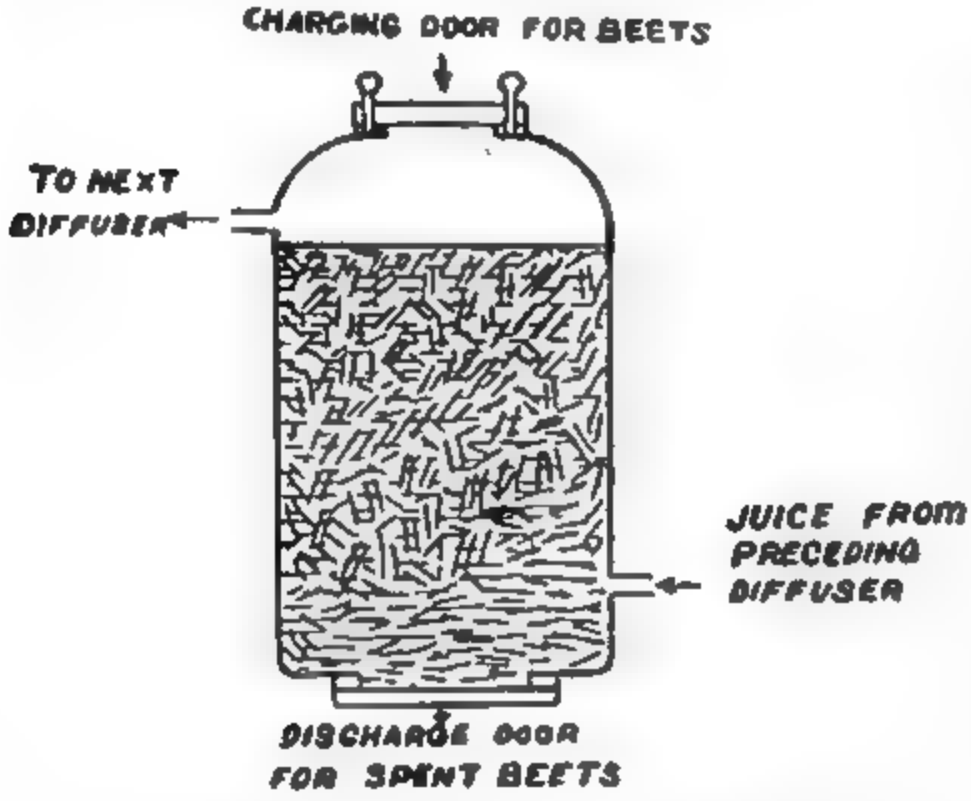


Fig 4. A Diffuser (Vertical Section).

The beets are cut into thin slices which are then immersed in warm water in vertical tanks or diffusers, as they are termed. Each of these has a capacity of from 4,000 to 8,000 litres, and is provided with a door at the top for charging with fresh slices, and another at the bottom for taking out the spent slices (Fig. 4). There is a battery of about 12 diffusers (Fig 5), arranged either in rows or in a circle, and working on the counter-current principle. The liquid enters each diffuser at the bottom and leaves it at the top as shown by arrows in Fig, 4, the slices remaining stationary. The diffuser No 1 (refer to Fig. 5)

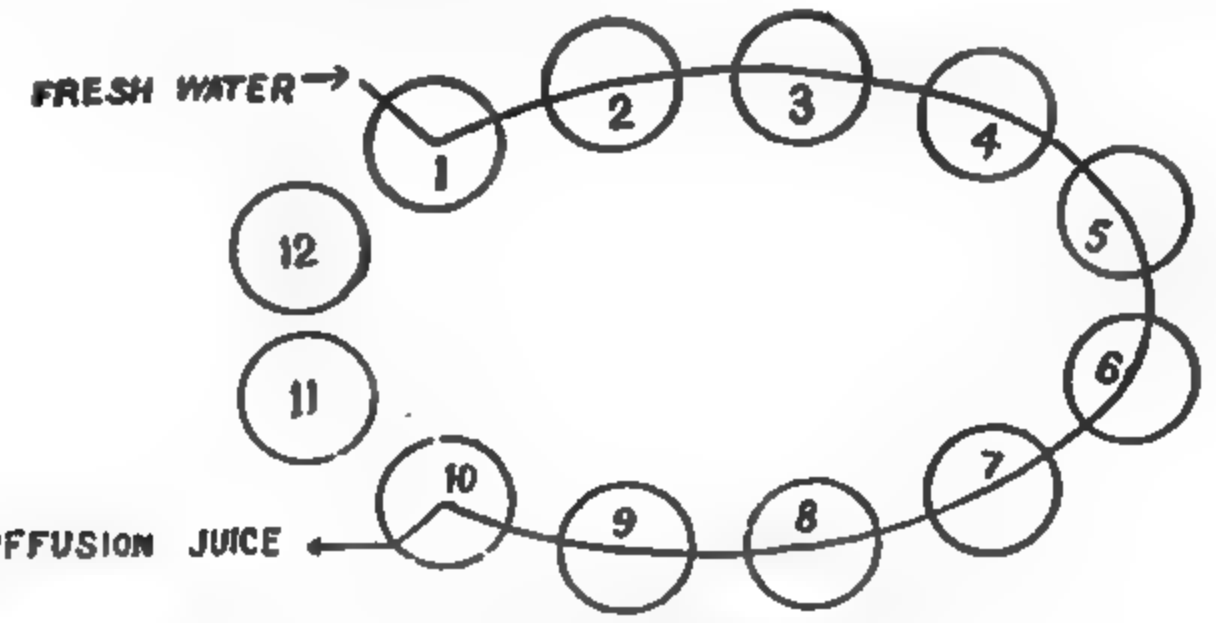


Fig. 5. Plan of a Circular Diffusion Battery.

[1] Fig. 3 illustrates the principle of the multiple-effect evaporator. The three evaporating pans P_1, P_2 and P_3 through which solution to be concentrated is continually circulated and kept at a constant level, are provided with three sets of heating coils, H_1, H_2 and H_3. The presure in P_1 is higher and that in P_3 lowest. Steam from a boiler is passed through H_1. This makes the lipuid in P_1 boil. The steam thus produced in P_1 passes out into the heater H_2 of the next pan P_2, and is hot enough to keep the liquid in this pan at the boiling point corresponding to the lower pressure. The steam produced by the boiling of the solution in P_2 passes into the heater H_3 of next pan and makes solution boil here also. The pressure in this last pan is kept very low by means of an exhaust pump. The saving of fuel achieved by multiple-effect evaporation may be as high as 80 per cent.

into which the fresh water enters, has been longest in action, so that the extraction here is practically complete. It is less complete in No. 2, still less in No. 3, and so on up to No. 10, which has just been filled with fresh beet slices. The water, after it has passed through diffuser No 1 (thus removing almost the whole of the sugar that the beet contained) passes on to diffusers Nos. 2, 3, 4, etc., until finally the solution having a high sucrose content passes into diffuser No. 10, containing the fresh slices. From here it takes up a further quantity of the sugar and thus we get a solution having as high a sucrose content as it is possible to get from the beets. This is known as the **diffusion juice.** The waste slices in diffuser No. 12, which previously acted as No 1 are being removed, while No. 11, which is being filled with fresh slices will be ready to act as the last diffuser in the following cycle, when No. 2 will become the first diffuser. The above operations are repeated round and round the battery, each diffuser in turn receiving fresh water at one end of the battery and fresh slices at the other end. The diffusion juice is treated in exactly the same manner as the cane juice, as already described.

Refining of Raw Sugar. The *raw sugar* obtained from cane or beet-juice has a brownish or yellowish colour. The process of refining the raw sugar consists of the following steps:

(1) *Affining.* This process has the object of removing adherent molasses, which envelops the grain, and may sometimes be very dark-coloured. The crystals are treated with a syrup of suitable strength, and then separated by means of centrifugal machines. The consistency of some raw sugars does not permit of affining.

(2) *Lime Treatment.* The crystals are then dissolved in water, and the solution treated with a little lime, followed by blowing in of carbon dioxide. This treatment has for its object the formation of a voluminous precipitate, which will carry down, by absorption, proteins and other colloidal impurities. The liquid is then passed through a filter press.

(3) *Decolorization.* The clear solution is now decolorized by filtering through animal charcoal. A "char filter" (Fig 6) has commonly the form of an iron cylinder, which may hold 20 tons or more of animal charcoal. The charcoal is uniformly packed on the filter cloth, and the liquid passed through it at a temperature of about 70°C.

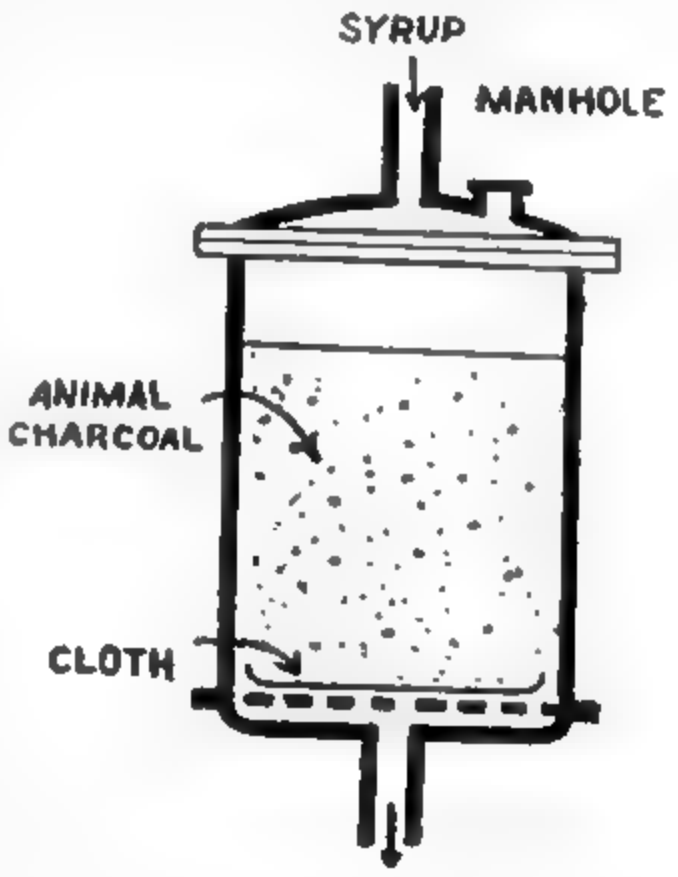


Fig. 6. Char Filter.

(4) *Crystallization.* The decolorized solution is once again concentrated in vacuum pans, until crystallization sets in. After allowing to cool, the crystals are separated by means of centrifugal machines, and may contain as much as 99·9% of sucrose.

Physical Properties. Cane-sugar crystallizes from water in colourless, anhydrous prisms, melting at about 160°C. It is readily soluble in water (3 parts of sugar in 1 of cold water), but only sparingly in alcohol. The aqueous solutions are *dextrorotatory.*

When cane-sugar is carefully heated, until it melts, and then allowed to cool, it solidifies to a pale-yellow, glassy mass known as **barley-sugar,**

which, on standing, gradually reverts to the crystalline state. When heated at 200°, it yields a brown product known as **caramel**, which is much used for tinting liqueurs and confectionary.

Reactions. (1) *Hydrolysis.* When warmed with dilute acids, sucrose is rapidly hydrolysed, yielding an equimolecular mixture of glucose and fructose:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The resulting mixture is *levorotatory*, as the fructose is more strongly levoratory than glucose is dextrorotatory. Since the solution before hydrolysis is *dextrorotatory*, the process is known as **inversion** and the mixture of fructose and glucose, so obtained, as **invert sugar**. The invert sugar forms a syrup, which is sweeter than cane-sugar, and is employed for making fruit preserves, *sherbets*, and as a substitute for honey.

As already mentioned, sucrose is fermentable by yeast, which contains the enzyme *sucrase* or *invertase* as well as *zymase*.

(2) *Acetylation.* When heated with acetic anhydride, sucrose gives an **octacetyl derivative.** This shows that the sucrose molecule contains eight hydroxyl groups.

(3) *Formation of Sucrates.* Sucrose forms well-defined metallic derivatives, called "sucrates". The best known of these is **di-strontium sucrate**, $C_{12}H_{22}O_{11}.2SrO$, which, being sparingly soluble, was once used in the separation of sugar from molasses.

(4) *Action of Concentrated Acids.* Concentrated sulphuric acid chars sucrose in the cold, producing carbon, carbon dioxide and sulphur dioxide. Concentrated nitric acid oxidizes it to oxalic acid.

(5) Sucrose does not give the characteristic properties of a monosaccharide. It is stable towards alkalies, does not reduce Fehling's solution or the ammoniacal silver nitrate solution, and does not react with phenylhydrazine, etc.

Tests. Sucrose may be identified by the various tests described in the following experiment:—

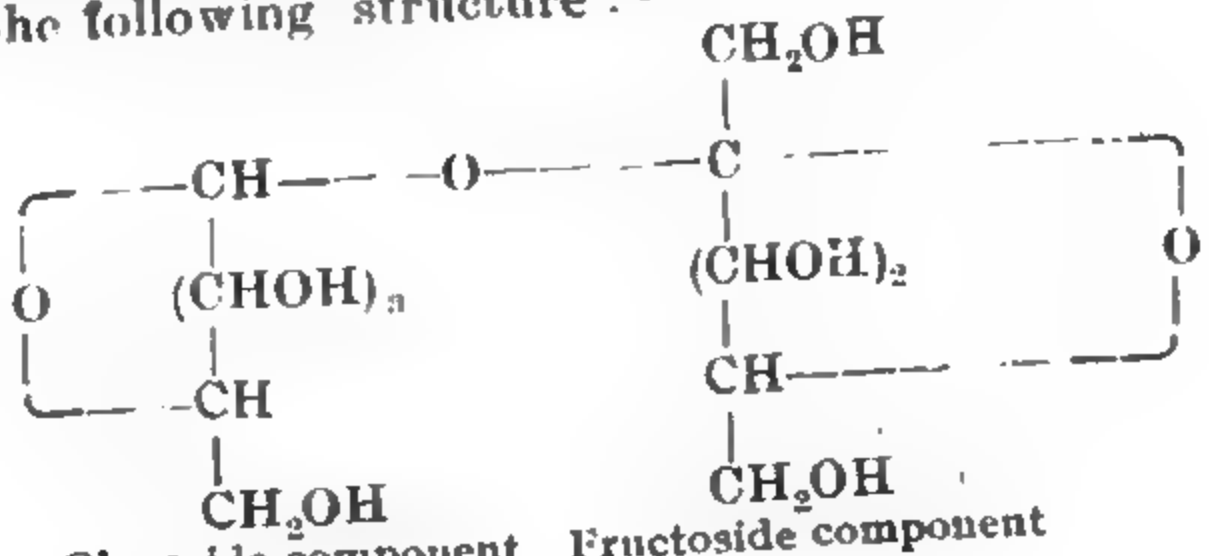
Expt. 3. *Tests of Sucrose.* (1) Heat a little of the dry sugar in a test-tube, until it melts and turns dark brown. Dissolve the product in water. Notice that a deep brown solution of caramel is produced.

(2) Take about 1 gram of sucrose in a test-tube, add 2 drops of water and about 1 c. c. of concentrated sulphuric acid. Warm, if necessary. A black, porous mass of carbon etc., is obtained.

(3) Show that sucrose does *not* reduce Fehling solution.

(4) Boil some cane-sugar for some time with dilute hydrochloric acid in a boiling tube. Alkalify the product with sodium hydroxide, add Fehling solution, and warm. Notice that the Fehling solution is reduced by the mixture of glucose and fructose produced in the first part of the experiment.

Constitution. Recent investigations have shown that the sucrose molecule has the following structure:—



Glucoside component Fructoside component

The discussion of the problem however, is beyond the scope of this book.

8. Starch. Next to cellulose, starch is the most abundant material found in the vegetable kingdom. In plant metabolism, starch occupies a central position among the carbohydrates, being transformed by enzyme action either into the simpler mono- or disaccharides, or into the more complex gums and celluloses. Starch occurs particularly in potatoes, wheat, maize, rice and the pith of the sago palm. In these the starch is stored as microscopic granules, the shape and size of which are characteristic of the source of the starch (Fig. 7). The granules, when examined under the microscope are found to consist of an inner nucleus, or "hilum" around which are arranged a number of concentric layers or 'striæ.' The hilum is the oldest, *i.e.*, the first formed, portion of the grain, while the striae represent layers of different density, some of them containing more or less water than others. No two species of plants are found to give exactly identical starches. The potato starch has the largest granules, (0·05 to 0·01 mm. diameter) which possess a characteristic, mussel-like appearance (0·003 to 0·007 mm. diameter). They have a tendency to coalesce into larger granules, Wheat starch consists of round, lens-shaped granules of 0·02 to 0·03 mm. diameter, while maize starch consists of characteristic, polyhedral granules with a dark centre and no visible striæ.

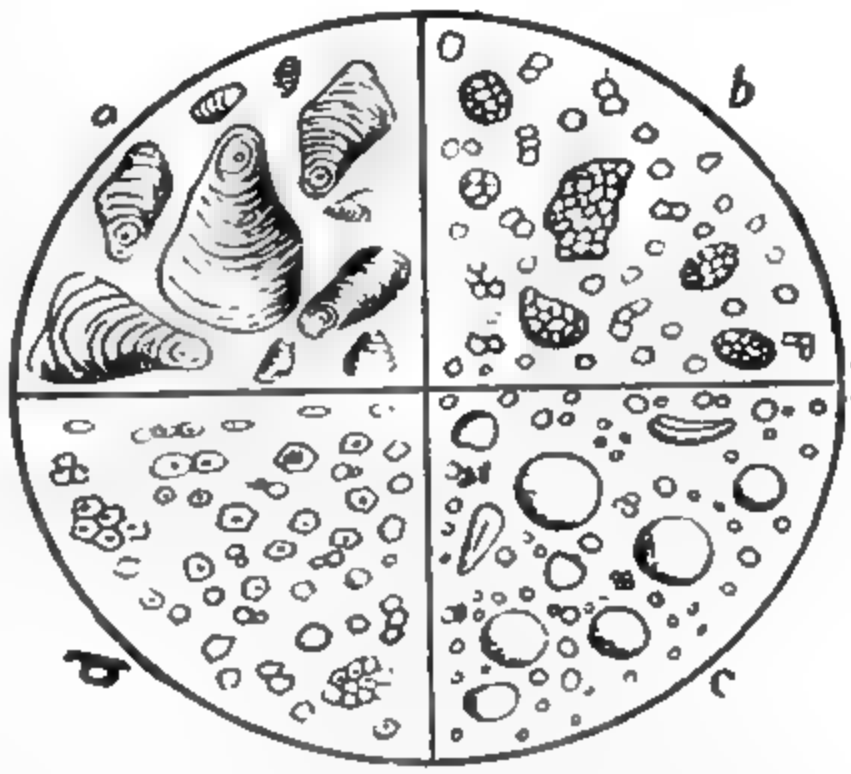


Fig. 7 Starch Granules, *a* Potato (*b*) Rice, (*c*) Wheat (*d*) Maize.

Manufacture. Starch manufacture is a very important industry. The two largest starch producing countries of the world are Germany and America. In Germany, starch is manufactured chiefly from potatoes and to a smaller extent from rice, while in America the chief source is maize. In India, Great Britain and other contries both wheat and rice are employed for this purpose.

The manufacture of starch is essentially a process of mechanical separation of this substance from other materials with which it is associated The procedure adopted differs in individual cases.

In the case of potatoes, after the preliminary washing to remove earth, sand and grit, the tubers pass to a rasping machine, in order to rupture the cells. The pulp thus obtained is carried by a fine stream of water on to fine-mesh brass sieves to separate the starch from coarser particles and fibrous material. The resulting milky liquid is run into tanks to separate fine sand and grit by settlement. It is then allowed to run slowly over long, shallow, wooden troughs, or gutters where the pure starch settles out, while the aqueous liquid, along with the impurities, passes off. The pure, white starch is washed from the gutters by a stream of cold water, and is pumped through filter presses. The starch thus obtained is in the form of a cake containing about 40 per cent of water.

In rice and other cereals, the starch is associated with varying proportions of protein or gluten material, which must be separated from starch. The portein present in rice is rendered soluble by very weak

caustic soda solution. This fact is untilzed in the production of starch from this sources.

In the case of wneat, the gluten forms an elastic mass with water, which it is not possible to remove by levigation. Hence, in this case the grain is first ground into flour, which is then made into dough with water. This is spread on a fine brass sieve, where a moving roller presses out the starch. This is levigated off by a spray of water. The resulting milky liquid is then treated as in the case of potatoes.

Properties. (1) *Physical Characters.* Starch is a white, hygroscopic powder, without any taste or smell As already described, the granules of starch from different plants are of different characteristic shapes and sizes.

(2) *Solubility.* Starch is insoluble in cold water. With hot water, it forms a paste, which is dextrorotatory

(3) *Reaction with Iodine.* The most characteristic reaction of starch is the production of a blue colour with iodine. This is employed as a test both for iodine and starch. The colour appears to be due to the absorption of iodine by starch, and not to the formation of any distinct compound.

(4) *Hydrolysis.* When starch is boiled with a dilute acid, it is converted first into dextrin and then into *d*-glucose. Since the conversion into glucose is quantitative, the reaction is utilized for the **estimation of starch**, the resulting glucose being titrated with Fehling's solution.

With certain enzymes, called **diastases** or **amylases**, starch is converted almost quantitatively into maltose The reaction is utilized in the industrial preparation of alcohol from starch

(5) *Action of Nitri Acid.* When treated with a mixture of concentrated nitric and sulphuric acids, starch gives **nitro starch,** which is a mixture of nitric esters (compare nitro-celluloses). Nitro-starch is used as a blasting explosive in the United States.

Uses (1) *As Food.* Starch is one of the essential constituents of our food, its function is chiefly to produce the bodily heat. We use starch in the form of corn-flour, arrow root, sago, *sooji*, and a constituent of bread : macaroni, *phirni*, *dalia*, potatoes and many other food articles

(2) *As a source of Glucose and Alcohol.* Starch finds extensive application in the manufacture of "starch syrup", "corn-syrup", glucose and alcohol.

(3) *As an Adhesive.* Starch paste is much used in book-binding and for other purposes By heating starch at about 180°, or by heating starch paste with a little nitric acid, we get a thick, gumlike product, which possesses powerful adhesive properties. This is known as **dextrine** or **British gum**, and is much used instead of the more expensive gum-arabic as an adhesive, for paper lables, stamps, envelopes, etc, The well-known adhesive, called "Gloy", mixture of dextrine starch and magnesium chloride.

(4) *In Laundries* Rice starch is extensively used by washermen for stiffening linen. The gelatinized starch is applied to the cloth, and is converted by passing over it a hot iron, into a shiny, stiff layer of dextrine.

9. Cellulose. Cellulose is the most complex polysaccharide known. It is widely distributed in the vegetable kingdom, and forms the fundamental constituent of cell walls of plants and skeleton of all vegetable tissues. Cotton, jute: hemp, flax, paper, wood, *etc.*, are all different forms of cellulose, containing small amounts of mineral matter which is left behind when these substances are burnt.

Preparation. Pure cellulose may be obtained from cotton, wool, flax or paper. The material is treated successively with dilute hydrochloric or hydrofluoric acid (to remove mineral matter), water alcohol and ether. The cellulose which is very stable towards dilute acids and alkalies, is thus obtained as a white, amorphous mass.

Cotton and linen cloths consist almost entirely of cellulose. The finest Swedish filter paper, got by extracting ordinary filter paper with hydrochloric acid is almost a chemically pure form of cellulose.

Properties (1) *Physical Characters.* Cellulose, like starch, possesses an organized structure, and occurs, in the form of hollow fibres, the appearance and dimensions of which are characteristic of their particular source. It is because of this structural peculiarity that cellulose forms the basis of the paper and the textile industries.

(2) *Solubility.* Cellulose is insoluble in all the ordinary solvents, but dissolves in **Schweizer's reagent** (ammoniacal solution of cupric hyroxide), forming a colloidal solution, from which the cellulose may be recovered as a gelatinous precipitate by the adition of an acid.

(3) *Hydration.* When cellulose is treated with dilute acids or comminuted mechanically with water (as in paper making), it is converted into a hydrated cellulose or **hydrocellulose.**

(4) *Hydrolysis by Concentrated Acids.* When cellulose is treated with cold, concentrated sulphuric acid, it swells up and passes gradually into solution. On adding water to this solution, a starch-like substance, called **amyloid,** is precipitated. On prolonged treatment with concentrated sulphuric acid, followed by boiling of the diluted liquid, cellulose undergoes complete hydrolysis, giving first dextrin and finally *d*-glucose.

(5) *Action of Alkalies.* Though cellulose is remarkably resistant to dilute alkalies, with a 15 to 20 per cent solution of caustic soda its ribbon-like fibre, having reticulated walls, swells up into a smooth-walled cylinder. This fact was noted in 1884 by John Mercer. Five years later, H.A. Lowe observed that if a cotton fabric, while immersed in alkali, be subjected to simultaneous stretching, to counteract the contraction consequent on the swelling it acquires a characteristic silky lustre. The process is known as mercerization, and is employed industrially on a large scale.

Uses. Cellulose is one of the most important substances known to us. It finds many applications such as the manufacture of cloth, paper, explosives, artificial silk, films, lacquers, celluloid, etc.

QUESTIONS

1. What are carbohydrates? Classify them. Describe methods of preparation of glucose and its reactions with phenylhydrazine. Give its structural formula.
(Punjab Inter., 1945)

2. State the chief properties of the principal groups of carbohydrates. Glucose is said to be an aldehyde and fructose a ketone. How would you confirm these statements?
(Punjab, Inter., 1924)

3. Outline the preparation of glucose from (*a*) starch, (*b*) sucrose, giving equations. Explain briefly how glucose reacts with Fehling's solution, ammoniacal silver nitrate, and phenylhydrazine. Are these reactions also given by fructose or sucrose? (*Punjab, Inter., 1928*)

4. By what properties and reactions would you distinguish a solution of cane-sugar from a solution of grape-sugar?

How would you demonstrate the production of grape-sugar from cane-sugar and starch respectively? (*Unit. Prov., Inter., 1925*)

5. What structural formula is given to glucose? From what hydrocarbon may this sugar be regarded as derived?

6. Briefly discuss the properties of glucose and fructose. In what ways do they differ and how can glucose be converted into fructose? (*Punjab, Inter., 1929*)

7. Describe the manufacture of cane-sugar. (*Punjab, Inter., 1929, 1930*)

8. Write equations to represent the following reactions :—

(*i*) Action of phenylhydrazine on glucose ;

(*ii*) Action of ammoniacal silver nitrate on glucose ;

(*iii*) Action of hot, concentrated hydrochloric acid on cane-sugar ;

(*iv*) Action of acetic anhydride on glucose.

9. You are given a solution which may be either (*a*) cane-sugar, (*b*) glycerine, (*c*) tartaric acid, state how you would proceed to identify it. (*Unit. Prov., Inter., 1927*)

10. You are given the following substances :—Cane sugar ; oxalic acid ; starch and urea. Mention the tests by which you would identify each substance. (*Unit. Prov., Inter., 1931*)

11. What is starch? Name three different sources from which it is obtained on a commercial scale. Give one characteristic test by which this substance can be identified. What different uses is starch put to?

12. What is cellulose? Give its chief properties and uses.

CHAPTER 23

DERIVATIVES OF CARBONIC ACID

1. Carbonic Acid Derivatives. The unstable acid present in an aqueous solution of carbon dioxide is known as *carbonic acid*. The anhydride of carbonic acid, *i.e.*, *carbon dioxide*, and its metallic salts, known as *carbonates* and *bicarbonates* are described in text-books of inorganic chemistry. Some of the derivatives of carbonic acid that are of interest to the organic chemist are described in this chapter. The following scheme will serve to illustrate the relationship between the acid and its more important derivatives :—

$O=C<^{OH}_{OH}$ Carbonic Acid

$O=C<^{OC_2H_5}_{OC_2H_5}$ Ethyl Carbonate

$O=C<^{Cl}_{Cl}$ Carbonyl Chloride

$O=C<^{OH}_{NH_2}$ Carbonic Acid

$O=C<^{NH_2}_{NH_2}$ Carbamide (Urea)

The esters of carbonic acid are obtained by the action of alkyl iodides on silver carbonate, or of carbonyl chloride on alcohols They are pleasant smelling liquids soluble in which they gradually decompose.

Being a dibasic acid, carbonic acid gives rise to *two* **amides,** the monoamide, known as *carbamic acid*, is of far less importance than the diamide, *urea*.

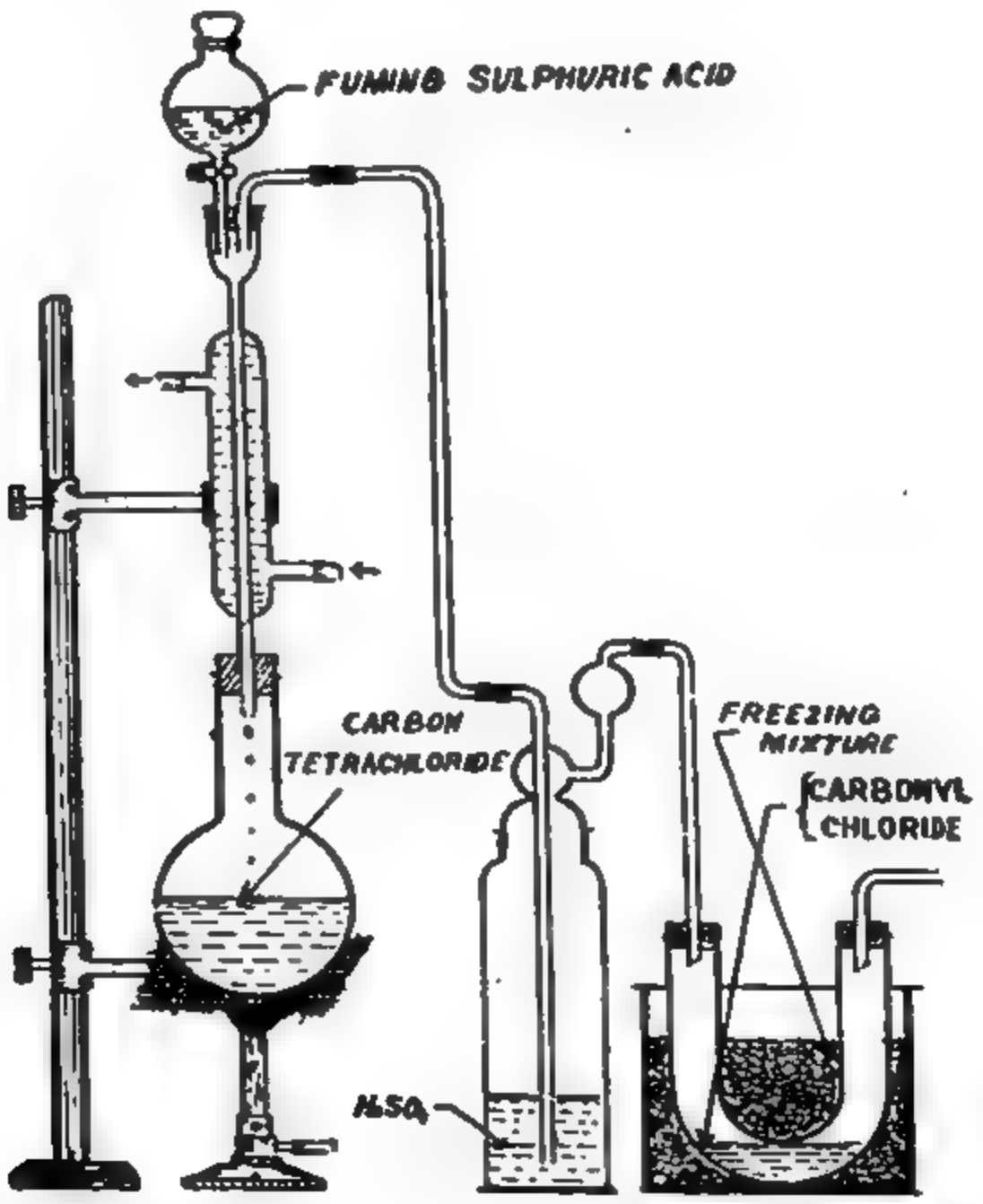


Fig. 1. Preparation of Carbonyl Chloride from Carbon Tetrachloride.

2. Carbonyl Chloride, *Phosgene*, $COCl_2$. This compound is produced when carbon monoxide and chlorine combine together in the

presence of sunlight or activated charcoal as a catalyst :

$$CO + Cl_2 \rightleftharpoons COCl_2$$

The reaction is highly exothermic, and is consequently favoured by low temperatures (below 350°).

The most convenient method of preparing carbonyl chloride consists in dropping 80 per cent fuming sulphuric acid (120 c.c.) into boiling carbon tetrachloride (100 c.c.) contained in a flask provided with a reflux condenser and a dropping funnel (Fig. 1).

The gas set free is washed with concentrated sulphuric acid and condensed in a U-tube immersed in a freezing mixture. The equation representing the reaction is as under :—

$$CCl_4 + 2SO_3 \longrightarrow COCl_2 + S_2Cl_2O_5$$

Carbonyl chloride is a colourless gas with a penetrating and suffocating odour, and is very poisonous. It can be readily condensed to a liquid (*b. p.* 8°).

Reactions :—The reactions of carbonyl chloride show that it is the chloride of carbonic acid :—

(1) It is gradually decomposed by water, yielding hydrochloric acid and carbon dioxide.

$$OC{<}^{Cl}_{Cl} + 2H.OH \longrightarrow OC{<}^{OH}_{OH} + 2HCl$$

Unstable

$$OC{<}^{OH}_{OH} \rightarrow H_2O + CO_2$$

(2) When treated with alcohol, it first forms ethyl chloroformate,

$$OC{<}^{Cl}_{Cl} + H\,OC_2H_5 \rightarrow OC{<}^{OC_2H_5}_{Cl} + HCl.$$

and finally ethyl carbonate.

$$OC{<}^{OC_2H_5}_{Cl + H\,OC_2H_5} \rightarrow OC{<}^{OC_2H_5}_{OC_2H_5} + HCl.$$

(3) With ammonia, it gives *urea* the diamide of carbonic acid.

$$OC{<}^{Cl + H\,NH_2}_{Cl + H\,NH_2} \rightarrow CO{<}^{NH_2}_{NH_2} + 2HCl.$$

Urea

Use. Carbonyl chloride is much used in the manufacture of di- and triphenyl-methane dyes, and is placed on the market either in the liquid state or in benzene solution. It is highly poisonous, and has, for that reason, been used in warfare.

3. Urea, *Carbamide*, $NH_2.CO.NH_2$. Urea is the diamide of carbonic acid, HO.CO.OH.

Occurrence. Urea occurs in the urine of mammals, a fully grown man excreting about 30 grams per day.

Preparation. (1) *Separation from Urine.* Urea may be obtained from urine by evaporation to a small bulk, and adding nitric acid, when urea nitrate separates out as a crystalline precipitate. This, after suitable purification, is decomposed with barium carbonate to recover urea.

(2) *By Isomerization of Ammonium Cyanate* (Wohler's method). Urea is generally prepared in the laboratory by Wholer's method, *viz.*, by evaporating an aqueous solution of ammonium sulphate and potassium cyanate. The ammonium cyanate, formed by the double decomposition between the two salts,

$$2KOCN + (NH_4)_2SO_4 \rightleftharpoons 2NH_4OCN + K_2SO_4$$

gets converted into urea by intramolecular rearrangement

$$\underset{\text{Ammonium cyanate}}{NH_4OCN} \rightleftharpoons \underset{\text{Urea}}{NH_2.CO.NH_2}$$

Expt. 1. *Preparation of Urea* :—

Potassium cyanide, 50 gm.
Red lead, 150 gm.
Ammonium sulphate, 50 gm.

Melt the potassium cyanide in an iron tray on a blow-pipe flame, and add the red lead in small quantities at a time. The cyanide is oxidized to the cyanate :—

$$4KCN + Pb_3O_4 \rightarrow 4KCNO + 3Pb$$

Allow the fused mass to cool, extract with boiling water, filter and add the ammonium sulphate. Evaporate the solution to dryness on a water bath, when ammonium cyanate (produced by double decomposition between potassium cyanate and ammonium sulphate) undergoes isomerization to urea.

The urea is extracted with hot alcohol, and the solution evaporated to obtain crystals of urea.

(3) It may also be synthesized by the action of ammonia on ethyl carbonate or carbonyl chloride (compare acetamide) :—

$$\underset{\text{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2NH_3 \rightarrow \underset{\text{Urea}}{CO(NH_2)_2} + 2C_2H_5OH$$

$$\underset{\text{Carbonyl chloride}}{COCl_2} + 4NH_3 \rightarrow \underset{\text{Urea}}{CO(NH_2)_2} + 2NH_4Cl$$

Manufacture. Urea is now manufactured on a very large scale by a recent process based upon the interaction of liquid ammonia and liquid carbon dioxide :—

$$CO_2 + 2NH_3 \rightarrow CO{<}\begin{matrix}NH_2\\NH_2\end{matrix} + H_2O$$

Uses (1) Synthetic urea is now extensively employed as a fertilizer in agriculture.

(2) Another use of urea is in the manufacture of synthetic resins (made by condensing urea with formaldehyde), which are employed in making unbreakable ornaments, light fittings, table ware, etc.

Physical Properties. Urea is a white solid, which crystallizes from water in long prisms (Fig. 2, *A*). It melts at 132°, and is soluble in water and in alcohol.

Reactions. Urea possesses the general chemical behaviour of an amide. Its more important reactions are :—

(1) *Basic Nature.* Urea is a weak, monacid base, and forms crystalline salts with strong acids, the two most characteristic of these being urea nitrate, $(NH_2.CO\,NH_3)NO_3$, and urea oxalate, $(NH_2.CO.NH_3)_2C_2O_4$.

These are obtained as crystalline precipitates by adding concentrated nitric acid, or a

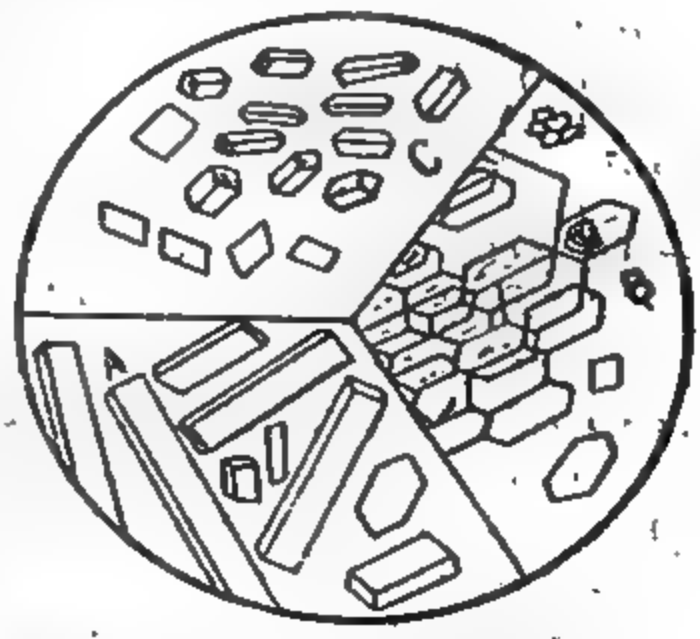


Fig. 2. (*A*) Urea. (*B*) Urea nitrate, (*C*) Urea oxalate.

saturated solution of oxalic acid, to a concentrated solution of urea. When examined under the microscope, the nitrate is seen to consist of rhombic, six-sided plates, which are often imbricated (like tiles) while the oxalate forms short rhombic prisms (Fig. 2, *B* and *C*).

(2) *Hydrolysis.* When heated with a dilute mineral acid or an alkali, urea is hydrolysed to give ammonia and carbonic acid :—

$$NH_2.CO.NH_2 + 2H.OH \rightarrow 2NH_3 + H_2CO_3$$
$$H_2CO_3 \rightarrow H_2O + CO_2$$

The hydrolytic decomposition of urea by means of **urease**, an enzyme present in soya beans, is utilized in the estimation of urea (*see* below).

Action of Nitrous Acid. Urea is decomposed by nitrous acid with evolution of carbon dioxide and nitrogen :—

$$NH_2.CO.NH_2 + 2ON.OH \rightarrow 2N_2 + CO_2 + 3H_2O$$

(4) *Action of Sodium Hypobromite.* When treated with an alkaline solution of sodium hypobromite, urea is decomposed with evolution nitrogen, the carbon dioxide produced in the reaction being retained by the alkali :—

$$NH_2.CO.NH_2 + 3NaOBr \rightarrow N_2 + CO_2 + 2H_2O + 3NaBr$$
$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

This reaction is also utilized for the estimation of urea (*see* below).

(5) *Action of Heat.* When urea is heated in a dry tube, it first melts, and then begins to evolve ammonia. Finally, the mass solidifies, and a ring of sublimed cyanuric acid may be formed on the upper, cool portion of the tube.

The white residue consists mainly of **biuret**, which is produced by the condensation of two molecules of urea with the elimination of a molecule of ammonia :—

$$\underset{\text{Urea (2 molecules)}}{NH_2.CO\,NH_2 + H\,NH.CONH_2} \rightarrow \underset{\text{Biuret}}{NH_2CO.NH.CONH_2} + NH_3$$

On shaking the solid in the tube with water, the buiret dissolves. If the solution be poured off and tested with a few drops of sodium hydroxide and a drop of dilute copper sulphate, a purple coloration is developed (**biuret reaction**).

Expt. 2. *Test of Urea* :—

(*i*) Heat a few crystals of urea in a dry test-tube. Test the evolved gas with moist red litmus paper, and note its odour. When the mass has resolidified, dissolve it in cold water, and test the solution with two or three drops of caustic soda and a drop of copper sulphate ; purple coloration.

(*ii*) Warm some urea with sodium hydroxide ; ammonia is evolved.

(*iii*) Prepare a solution of urea in water, acidify it with hydrochloric acid, and add sodium nitrite solution ; effervescence owing to the evolution of nitrogen.

(*iv*) Prepare a concentrated solution of urea, divide into three parts, and test separately with (*a*) concentrated nitric acid, (*b*) saturated aqueous oxalic acid and, (*c*) 1 per cent mercuric nitrate. A white ppt. is formed in each case.

Estimation. (1) ***Hufner's Method***. This method for the estimation of urea consists in adding a known volume of solution containing urea to an excess of an alkaline solution of sodium hypobromite (Reaction 4). From the volume of nitrogen evolved, the amount of urea in the solution is calculated.

One of the forms of the apparatus used in this method is the **Doremus ureameter** (shown in Fig 3). The larger tube *A*, is filled with a cold, freshly prepared solution of sodium hypobromite, while the

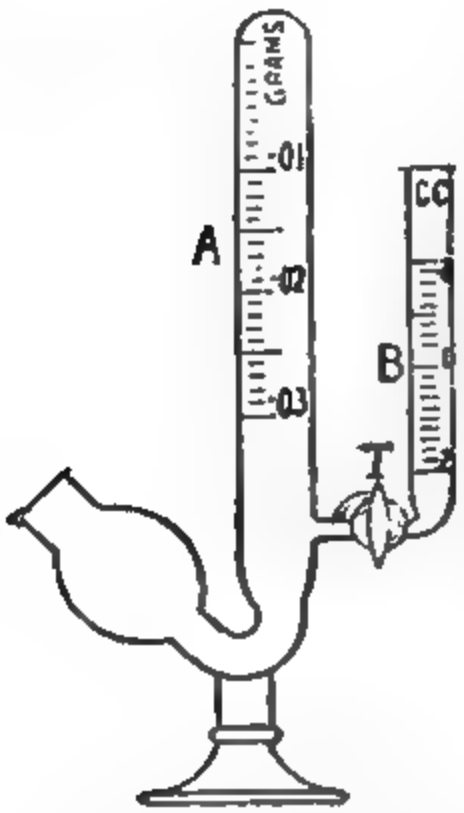


Fig. 3. Dormus Ureameter

smaller tube *B*, is charged with urine or dilute (about 2 per cent) urea solution to be examined. The tap *T*, is then carefully opened, and exactly one c.c. of the urea solution is admitted The volume of nitrogen that coll cts in the tube, *A*. is read, and gives directly the weight of urea per c.c. of the liquid.

(2) *By Urease.* Another very convenient method for estimation of urea is based on the action of an enzyme called urease, which occurs in soya beans. This transforms urea quantitatively into ammonium carbonate:

$$CO{<}^{NH_2}_{NH_2} + 2H_2O \rightarrow (NH_4)_2CO_3$$

The product is distilled with an excess of potassium hydroxide, the evolved ammonia is caught in an excess of standard acid, as in Kjeldahl's method for the estimation of nitrogen. The excess of the acid is then back-titrated with a standard alkali.

QUESTIONS

1. What is carbonyl chloride? How is it prepared and what is it used for?
2. How is urea commonly prepared? Give its important reactions, and discuss its constitution. (*Punjab, B. Sc., 1934*)
3. Write a note on the preparation and synthesis of urea Describe a method for the quantitative estimation of urea in solution. (*Calcutta, B. Sc., 1910*)
4. 20 c.c. of a liquid containing area, on treatment with alkaline sodium hypobromite yielded 43·05 c.c. of nitrogen measured at 18° and 742 mm. pressure. Given that in this reaction only 92 per cent of the nitrogen is evolved in the gaseous state, calculate the percentage of urea in the liquid. (*Ans.* 0·574 gm. per 100 c.c.)

PART III

AROMATIC COMPOUNDS

CHAPTER 24

THE COAL-TAR INDUSTRY

1. General. The parent hydrocarbon of the numerous aromatic compounds is benzene, just as methane is that of the aliphatic compoun ds. Certain of the substances derived from benzene were obtained originally from aromatic resins and oils. While the actual constitution of these compounds was not known, they all had a pleasant, "aromatic" odour ; hence they were grouped together as **aromatic compounds**. The term "aromatic" is now employed for all the benzene derivatives.

2 Destructive Distillation of Coal. The main source of the aromatic compounds is the tar obtained as a by-product in the destructive distillation of coal at temperatures above 1000°C. This is carried out either for the manufacture of coal-gas or of coke required for the metallurgy of iron and other metals.

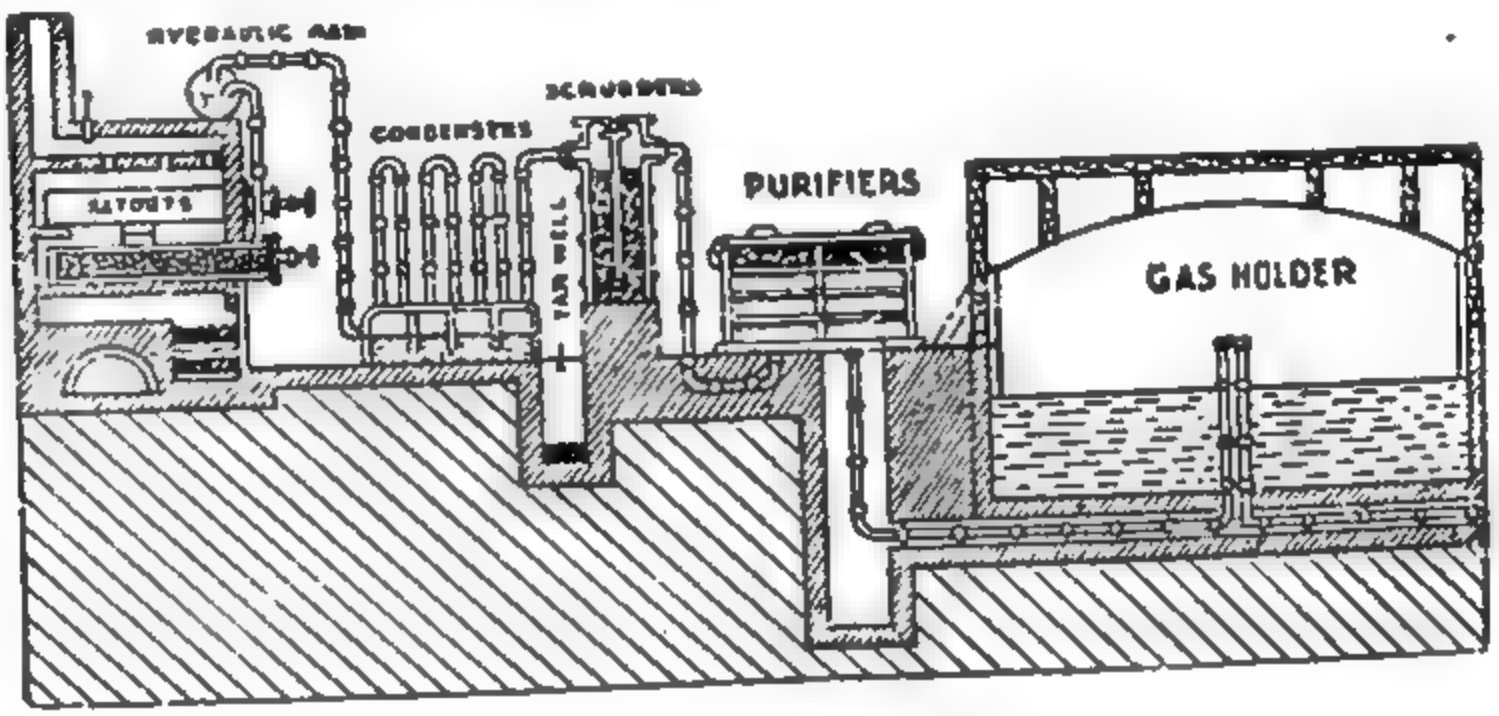


Fig. 1. Manufacture of Coal-Gas.

The plant employed in the manufacture of coal-gas is shown in Fig 1. Gas-coal (*i.e.*, coal rich in hydrogen and yielding a high proportion of gas) is heated in fire-clay retorts (shown on the left-hand side of the figure) heated by a coke fire. The volatile products bubble through wat r in a hydraulic main, where most of the tar gets condensed. The gas then passes through condensers or a series of air-cooled pipes, where the rest of the tar gets condensed. Next, the gas passes upwards through a scrubbing tower, packed with loose coke, down which water is sprayed. Here most of the ammonia and some of the hydrogen sulphide present in the gas is removed. It is then led into a purifier, containing trays filled with moist ferric hydroxide or lime, where the rest of the hydrogen sulphide is absorbed. The purified gas is collected over water in gas-holders, and delivered under pressure into distributing mains.

3. Fractional Distillation of Coal-Tar. Coal-tar is a thick, black liquid with characteristic acrid odour. It is an extremely complex

mixture of neutral; basic and acidic substances. The first are chiefly hydrocarbons of the aromatic series. From 5 to 10 % of the tar consists of naphthalene, and from 1 to 1·5 % of a mixture of benzene and toluene. Basic constituents, which are present only in small proportion include pyridine, quinoline and their homologues. The principal acidic constituent of tar is phenol or carbolic acid.

The separation of the various components of tar is effected by (*i*) fractional distillation, and (*ii*) chemical treatment.

The tar received from the gas works is run into a tank, and allowed to stand, until the ammoniacal liquor mixed with it has separated by gravity. The separation is facilitated, especially in the cold weather, by a steam coil laid in the tank. If the ammoniacal liquor is not completely removed before distillation, it would cause frothing in the still.

The plant employed for the distillation of coal-tar is shown in Fig 2. The tar-still is made of iron, and has a capacity of 20 to 30 tons. The top consists of a cast iron dome provided with (*i*) a manhole, *M*, (*ii*) an inlet pipe, *P*, for tar, (*iii*) a broad, curved vapour pipe, *V*, (*iv*) a thermometer tube, *T*, and (*v*) a safety valve *S*. The bottom of the still is concave, and rises to a considerable height. This ensures the distribution of heat into the interior of the mass of tar, and further, since the outlet pipe, *O*, is placed at the lowest point, it is also helpful in emptying the still at the end of the operation. The bottom is usually protected from direct contact with the flames by a brickwork arch, *A*. The still is provided with a steam-coil, through which superheated steam is blown towards the end of the operation, to facilitate the distillation of the heavy oil. The still is set in a furnace so that the flames play under the bottom, and about half-way up the height, through side-flues, in the brick setting.

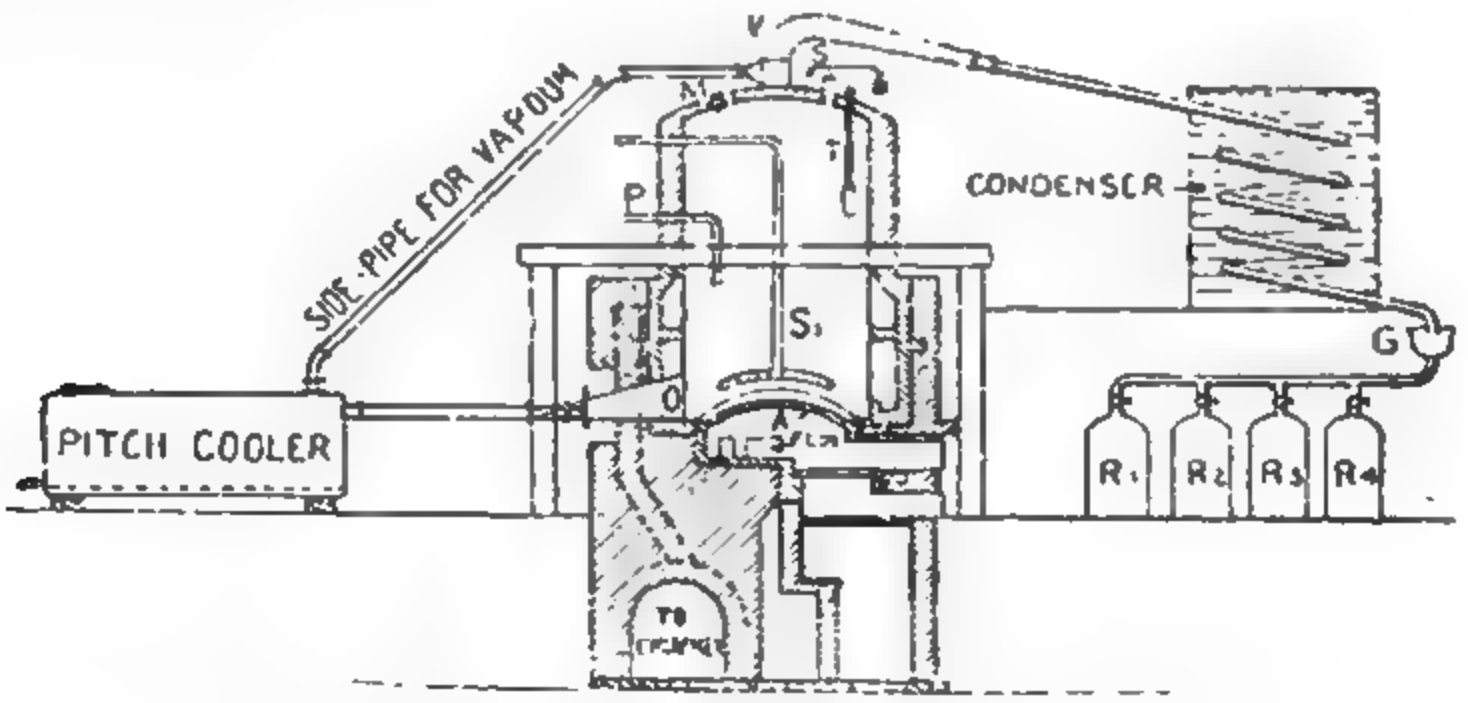


Fig. 2. Fractional Distillation of Coal-tar.

The condenser consists of an iron worm placed in a tank. The latter is provided with a steam pipe to warm the water if necessary. The various fractions are collected in separate receivers, the process being checked by occasionally noting the specific gravity of the distillate in a suitable outlet vessel, *G*.

The tar is run into the still while the latter is still hot from a previous operation. When the charging is about one-half completed, the heating is started and the fire is carefully controlled, till the cracking noise in the still ceases, which is an indication that the water has all been carried over. The fire can now be pushed, so that the distillat-

runs at the rate of 4 to 6 gallons per minute. The distillate is usually collected in the following *four* fractions :—

(1) **Light oil**, which is lighter than water and distils between 80° and 170°.

(2) **Middle oil**, or *carbolic oil*, which has approximately the same density as water, and distils between 170° and 230°.

(3) **Heavy oil**, or *creosote oil*, which is heavier than water, and distils between 230° and 270°.

(4) **Green oil** or *anthracene oil*, which is green in colour, and distils between 270° and 400°.

Towards the end of the operation, superheated steam is admitted into the still to aid distillation, which is carried on until the distillate becomes resinous.

The fire is now drawn, and the residue in the still, known as pitch, is run, while still hot[1], into the *pitch cooler* — a closed tank provided with a manhole, the latter being closed with a loosely fitting lid, which while it acts as a safety valve, prevents free access of air[2]

4 Isolation of Benzene, Toluene and Xylenes. Benzene, toluene and xylenes are isolated from the light oil, which contains, in addition to the aromatic hydrocarbons (neutral), appreciable quantities of basic substances (*e.g.*, pyridine) and acid substances (phenols). The various steps of the procedure are :—

(1) *Dilute Acid Treatment.* The light oil is first agitated with dilute sulphuric acid in a lead lined, cone-bottomed tank. The acid layer, after being allowed to settle, is drawn off.

(2) *Alkali Treatment.* The oil, freed from the basic substances, as above, is next treated with sodium hydroxide solution which removes phenols. The alkali layer, after being allowed to settle, is run off.

(3) *Concentrated Sulphuric Acid Treatment.* The oil is now agitated with about 5 per cent of concentrated sulphuric acid, the temperature being kept low. By this means *thiophene* and *olefines* are dissolved, and more complex substances are charred. After running off the acid tar, the oil is washed with a little sodium hydroxide solution to remove sulphur dioxide, and finally washed with water.

(4) *Fractionation.* The neutral oil thus obtained is now redistilled, using a still (*see* Fig. 3) provided with a rectifying column and cooler for fractional condensation. The latter consists of a number of chambers (*C*, *C*) surrounded by a water-bath, which may be kept at any desired temperature. Here the high-boiling components get condensed and flow back into the still head to be further fractionated, while the more volatile components pass on to the water-cooled worm condenser.

In the fractionation of light oil the following fractions are collected in the first instance.

(1) *90 per cent benzol*, up to 95° ;
(2) *50 per cent benzol*, up to 125° ;
(3) *Solvent naphtha*, up to 170°.

The residue in the still, which contains naphthalene and heavy oil,

---

1 The still must be emptied while the pitch is still sufficiently hot to drain out completely ; if any of it is left in the still, the heat of the brickwork will convert it into coke, which sticks very firmly to the still bottom, and prevents heating of the next charge.

2 If a free access of air is permitted, the hot tar would catch fire.

is added to the second fraction from the tar still.

Note. The terms "90 per cent benzol" and "50 per cent benzol" do *not* Indicate the benzene content, but refer to the proportion by volume of the fraction that distils up to 100°C. The two fractions consist of a mixture of benzene and toluene, the 90 per cent benzol containing about 70 per cent of benzene and 50 per cent benzol about 46 per cent of it.

(5) *Refractionation.* The 90 per cent benzol and 50 per cent benzol are now submitted to systematic refractionation in order to obtain pure benzene (*b.p.* 80°) and pure toluene (*b.p.* 110°). The residue, which consists of xylenes and higher hydrocarbons, is mixed with solvent naphtha.

The solvent naphtha consists of xylenes and higher members. It is used as a solvent for resins and rubber. If necessary, it may be refractionated to get the xylenes and higher hydrocarbons.

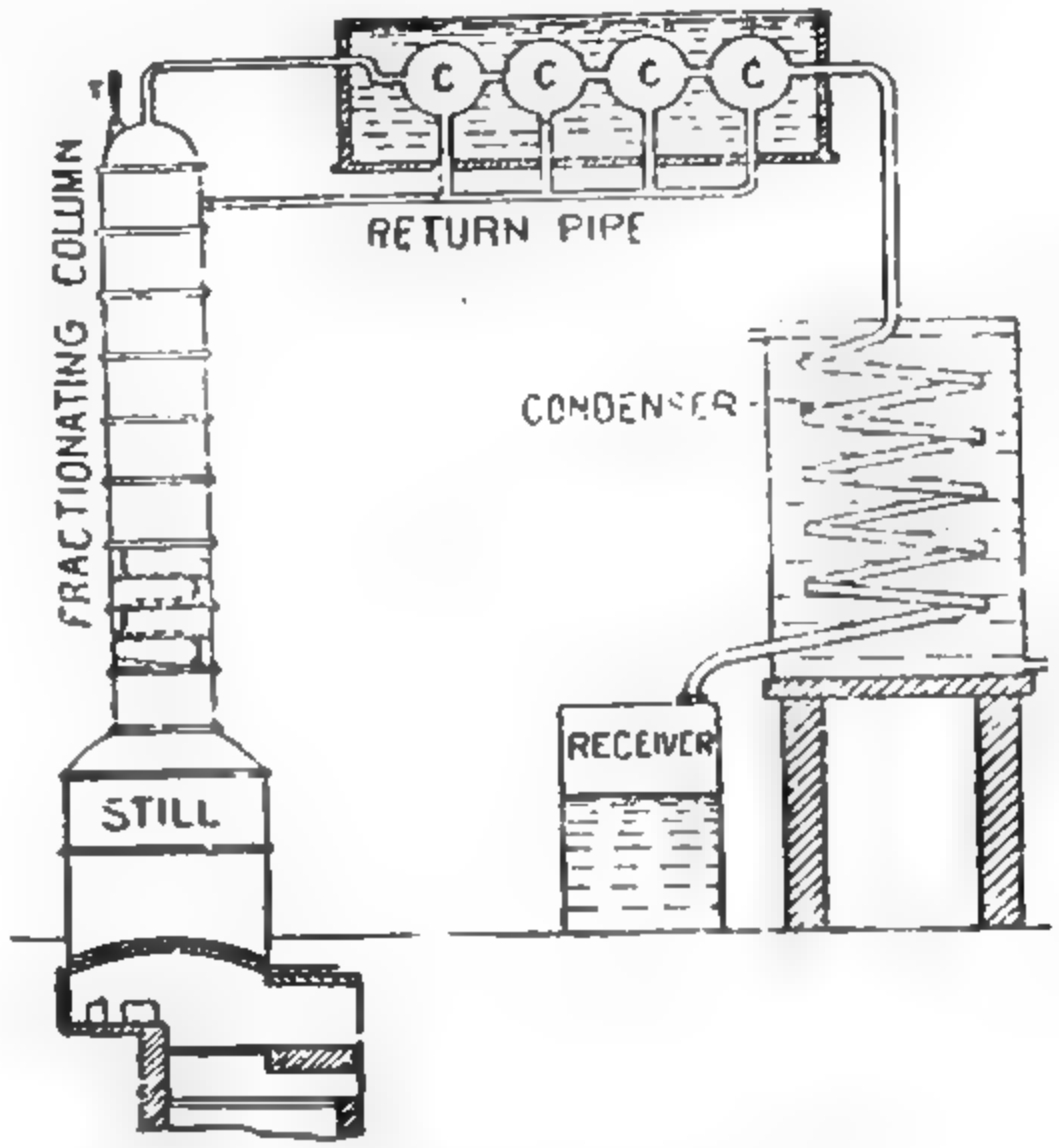


Fig. 3. Plant for the Fractionation of Light Oil.

5. Isolation of Phenol. Phenol or *carbolic acid* is separated from middle oil, which consists mainly of naphthalene (an aromatic hydrocarbon) and phenols. The oil is first allowed to cool, when most of the naphthalene crystallizes out. This is removed by centrifugation.

The oily mother liquor from which naphthalene has been removed is agitated at a temperature of about 60° with a sufficient quantity of dilute sodium hydroxide solution, which dissolves out the phenols. The alkaline liquid, containing sodium phenates, is subjected to steam distillation to remove the hydrocarbon impurities, and is then treated with sulphuric acid or carbon dioxide to set free the phenols. The latter are then submitted to fractional distillation in column stills. Three fractions are collected. The first, collected at 180° to 183°, consists of crystallizable **phenol**, the second does not contain a sufficient quantity of phenol to crystallize, while the third one consists principally of *cresols*.

QUESTIONS

1. Describe the distillation of coal-tar. What primary products are obtained in the process, and to what treatment are they respectively put?
2. How would you obtain a specimen of pure benzene from coal-tar? (*Punjab, Inter., 1923*)
3. Explain the terms, 90 per cent benzol' and '50 per cent benzol'.
4. Describe in detail isolation of (*a*) toluene, and (*b*) phenol from coal-tar.
5. Write an essay on the coal-tar Industry.
6. Describe precisely what happens when coal-tar is subjected to fractional distillation. How would you isolate benzene, toluene and phenol from the crude distillate in a state of approximate purity? What impurity is usually present in coal-tar benzene? How is it detected and removed? (*Calcutta, B.Sc., 1934*)
7. Show the industrial importance, and describe the fractional distillation of coal tar. How would you obtain a pure sample of benzene from it? (*Punjab, Inter., 1944*)

CHAPTER 25

BENZENE

1 History. Benzene, C_6H_6, the parent hydrocarbon of the aromatic series, was first isolated by Faraday in 1825 from oil-gas. Its presence in coal-tar was discovered in 1845 by A. W. Hofman.

2. Manufacture. Benzene, as already described is isolated on a large-scale from the *light-oil* fraction of the coal-tar distillation by systematic refractionation.

3. Laboratory Preparation. (1) A sample of pure benzene may be obtained in the laboratory from the commercial "90 per cent benzol" as follows :

(*a*) The commercial product is subjected to repeated fractionation in a flask provided with an efficient column, the fraction boiling at 80° to 81° being collected separately.

(*b*) The fraction collected at 80° to 81° is cooled by means of a freezing mixture, when crystals of almost pure benzene separate out, the impurities being, for the most part, left in the mother liquor. The crystals are quickly filtered, and pressed in the cold between layers of filter paper They may be melted and the process of cooling repeated, if necessary[1].

(*c*) The product still contains about half a per cent of thiophene, a sulphur compound whose boiling and freezing points are remarkably near to those of benzene. To remove this impurity, the benzene is shaken for a long time with *cold*, concentrated sulphuric acid, which sulphonates and dissolves out thiophene, while benzene remains practically unaffected. The treatment with sulphuric acid is continued, until the product ceases to give a blue coloration with concentrated sulphuric acid and a trace of isatin (**indophenine reaction**). It is then redistilled.

Expt. 1. *Indophenine Reaction of Thiophene.* Dissolve a crystal of *isatin* in about 5 c.c. of cold concentrated sulphuric acid. Add about the same volume of commercial benzene. A deep-blue coloration (indophenine) will be produced.

Repeat the test, using benzene obtained from sodium benezoate (Expt. 80). See that no blue colour is developed.

(2) A sample of pure benzene may be obtained in the laboratory by distilling benzoic acid or sodium benzoate with soda lime (compare the preparation of methane from sodium acetate) :

$$\underset{\text{Sodium benzoate}}{C_6H_5COONa} + NaOH \rightarrow \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

Expt. 2. Mix equal quantities of dry sodium benzoate and soda-lime and distil the mixture from a retort connected to a Liebig condenser. Benzene passes over

4. Synthesis. Benzene may be synthesized from its elements through acetylene (*p.* 71). The latter hydrocarbon when heated to a dull red heat is partially converted into benzene :—

$$\underset{\text{Acetylene}}{3C_2H_2} \rightarrow \underset{\text{Benzene}}{C_6H_6}$$

Expt. 3. Introduce acetylene into a hard-glass tube closed at one end and

[1] This is ascertained by distilling the product; the boiling point should remain constant at 80°.

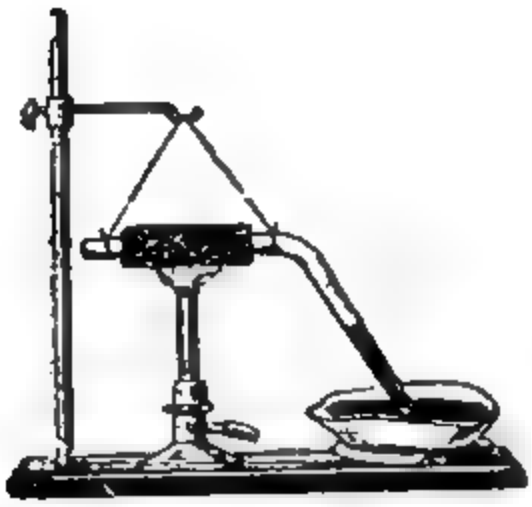


Fig. 1. Conversion of Acetylene into Benzene.

bent at an angle of about 120°, the tube being previously filled with mercury (Fig. 1.) Mark the position of mercury in the tube, and wrap a piece of copper gauze round a portion of the horizontal limb. Heat the gauze carefully with a bunsen burner. Fumes will soon appear in the tube, and minute drops of benzene will condense on the colder parts of the tube. After about 15 minutes heating, allow the tube to cool; the mercury will rise *above* its original level.

5. Properties. Benzene is a colourless, highly refractive, mobile liquid of a peculiar, aromatic odour. It boils at 80·4°. When cooled in a freezing mixture, it solidifies to a crystalline mass, melting at 5·4°.

Benzene, like other hydrocarbons, is insoluble in water, but is perfectly miscible with alcohol, ether, and petroleum It dissolves resins, fats, sulphur and other substances insoluble in water, and is, on this account, extensively employed as a solvent.

As shown by its formula, benzene is as rich in carbon as acetylene and burns with a luminous, smoky flame.

In its **chemical reactions,** benzene differs entirely from the aliphatic hydrocarbons. The following are the chief reactions which characterize benzene :—

(1) *Nitration.* When benzene is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid, it gives nitrobenzene:—

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 \rightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

(2) *Sulphonation.* When heated with concentrated sulphuric acid, benzene gives benzene sulphonic acid.

$$\underset{\text{Benzene sulphonic acid}}{C_6H_6 + H_2SO_4 \rightleftharpoons C_6H_5.SO_2OH} + H_2O$$

(3) *Chlorination and Bromination.* Action of chlorine and bromine on benzene is interesting, and two different classes of compounds are produced according to the condition of the experiment. In the presence of halogen carrier (iron, aluminium, or iodine) and in the cold *substitution* occurs, with the production of chloro-and bromo-benzenes :—

$$\underset{\text{Chlorobenzene}}{C_6H_6 + Cl_2 \rightarrow C_6H_5Cl} + HCl$$

$$\underset{\text{Bromobenzene}}{C_6H_6 + Br_2 \rightarrow C_6H_5Br} + HBr$$

At higher temperatures and in the absence of a catalyser *addition* of the halogen occurs, and we get benzene hexachloride, $C_6H_6Cl_6$, and benzene hexabromide. $C_6H_6Br_6$.

(4) **Friedal and Crafts' Reaction.** When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, the alkyl group enters the benzene nucleus, and we get a benzene homologue :

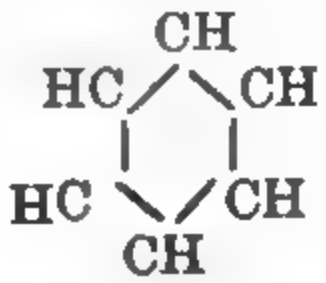
$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \rightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + HCl$$

6. Detection. Besides the physical constants of the hydrocarbon, a characteristic test of benzene is its reaction with nickelous cyanide. An ammoniacal solution of this substance yields with benzene a white, violet-tinted, crystalline compound of the formula $Ni(CN)_2.NH_3.C_6H_6$.

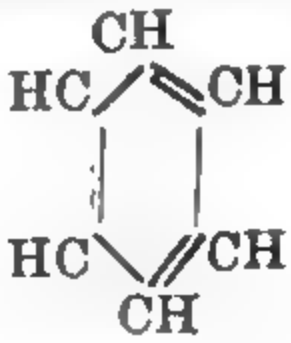
7. Uses. (1) The principal use of benzene is in the manufacture of nitrobenzene and other derivatives.

(2) It is employed as a solvent for resins, fats, etc.
(3) It is also used for dry cleaning of woollen clothes.

8. Ring Structure of Benzene. The molecular formula of benzene, as determined by combustion and molecular weight determination, is C_6H_6. The low proportion of hydrogen to carbon indicates that benzene, like ethylene and acetylene, should possess an unsaturated nature, but its properties are in direct opposition to this assumption. Thus, whereas unsaturated compounds readily form addition products with chlorine and bromine, are easily attacked by oxidizing agents, and at once react with Baeyer's reagent (a dilute alkaline solution of potassium permanganate), benzene does not possess these properties. It is, therefore, evident that the molecular structure of benzene must be entirely different from that of the open chain or or aliphatic hydrocarbons. From these considerations, and from the number of isomeric mono-and di- substitution products of benzene that exist, Kekule' concluded that *the molecule of benzene consists of a symmetrical closed chain of six carbon atoms, each of which is united with one atom of hydrogen* as shown below :—



The above formula accounts for only *three* of the four valencies of the carbon atoms. According to Kekule', each of the carbon atoms is linked to one of its two neighbours by a double bond as shown below :—



For the sake of convenience, the molecule of benzene is usually represented by hexagon, . It is understood that a hydrogen atom is present at each vertex, unless replaced by a substituent. Thus, nitrobenzene, aminobenzene, and benzoic acid are represented by the simple formulæ shown below :—

Nitrobenzene, $C_6H_5.NO_2$, or

Aminobenzene, $C_6H_5.NH_2$, or

Benzoic acid, $C_6H_5.COOH$, or

QUESTIONS

What is benzene ? Why is it an important compound ? Can benzene be obtained from an aliphatic hydrocarbon ? If so, how ?

2. From what source is benzene obtained on a commercial scale ? Describe the process concisely. How will you proceed to obtain a sample of pure benzene from sodium benzoate ? Draw a sketch of the apparatus that you will use, and write the equation representing the reaction.

3. How is benzene obtained in the laboratory ? Name the impurities present in the commercial product, and give methods to get rid of these impurities *(Punjab, Inter., 1925)*

4. Describe how pure benzene is obtained from coal-tar. *(East. Punjab., 1948)*

5. Discuss briefly the constitution of benzene *(Punjab, Inter., 1947)*

6. By what reactions is benzene distinguished from the hydrocarbons of the aliphatic series ? *(Punjab, Inter., 1921)*

7. Write equations to represent the following reactions :—

(*i*) Action of hot, concentrated sulphuric acid on benzene.

(*ii*) Action of chlorine on cold benzene in the presence of iron filings.

(*iii*) Action of methyl chloride on benzene in the presence of anhydrous aluminium chloride.

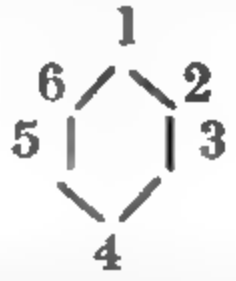
(*iv*) Action of heat on a dry mixture of sodium benzoate and soda-lime.

CHAPTER 26

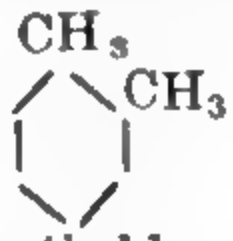
ISOMERISM AND ORIENTATION OF BENZENE DERIVATIVES AND ORIENTATING INFLUENCE OF SUBSTITUENTS

I. Isomerism of Benzene Derivatives. Owing to the equivalence of six hydrogen atoms, the mono-substitution products of benzene exist only in one form. Thus there is only one monochloro-benzene, C_6H_5Cl, one monobromobenzene, C_6H_5Br, and so on.

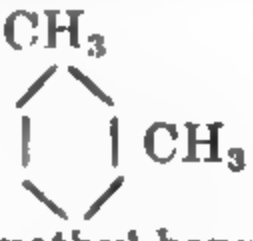
When two or more hydrogen atoms of benzene are replaced by substituents, the relative positions of the latter are best denoted by numbers as given below :—



The disubstitution products of benzene occur in *three* form as shown below in the case of xylenes (dimethyl-benzenes) :—



1:2-Dimethyl benzene
or *ortho*-Xylene



1:3-Dimethyl benzene
or *meta*-Xylene

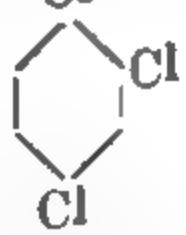
1:4-Dimethyl-
benzene or *para*-Xylene

The terms **ortho-, meta-, and para-,** are applied to 1 : 2, 1 : 3 and 1 : 4 compounds respectively. For the sake of brevity, they are denoted by the letters *o-*, *m-*, *p-*.

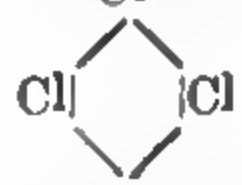
Even when the two substituents are different, the number of isomerides remains three. Thus, there are three chloromethyl-benzenes, three chlorobromobenzenes, and so on.

When three hydrogen atoms of the benzene nucleus are replaced, the case, however, is otherwise. Thus, trisubstitution products in which all the substituents are *identical*, exist in three forms, designated as shown below :—

Adjacent
or 1 : 2 : 3-
Trichlorobenzene



Unsymmetrical
or 1 : 2 : 4-
Trichlorobenzene



Symmetrical
or 1 : 3 : 5-
Trichlorobenzene

In case two of the three substituents are identical; as in $C_6H_3(OH)Br_2$, six isomerides are possible ; if all three be different, as in $C_6H_3(OH)ClBr$, the number of possible iosmerides becomes ten.

The tetra-substitution products of benzene, in which all the substituents are identical, also exist in three isomeric forms as shown below :

1 : 2 : 3 : 4-

1 : 2 : 3 : 5-

1 : 2 : 4 : 5-

When five or six atoms of hydrogen are replaced by identical substituents,

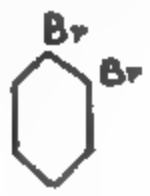
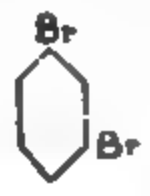
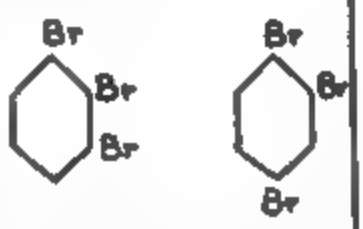
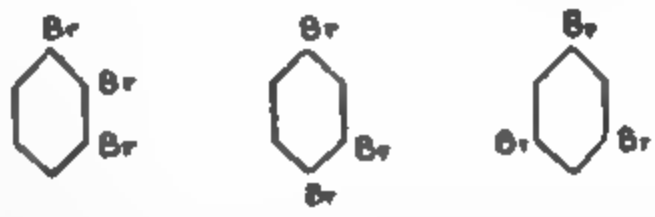
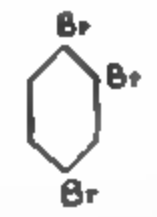
there is again only one compound possible. If the substituents be different, the number of possible isomers in each case becomes much higher.

2. Orientation of Benzene Derivatives. The term "orientation" signifies the determination of the relative positions of the substituents in the benzene nucleus. There are two different methods available:

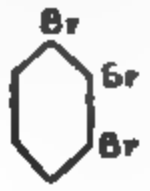
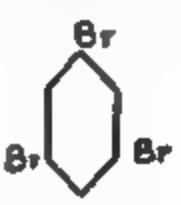
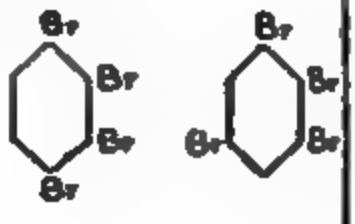
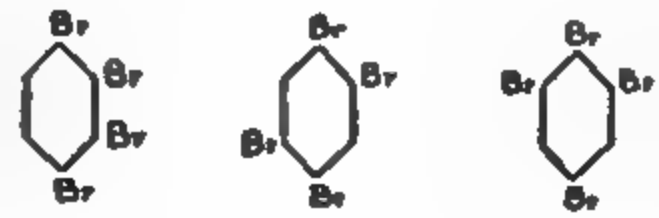
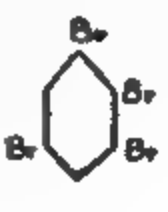
(1) **Relative Method.** In this method the compound with substituents in unknown positions, is converted into another having substituents in known positions, it being assumed that the first compound has its substituents in the same relative positions as the second.

Thus, if we want to determine whether a given xylene is the *ortho-*, *meta-*, or *para*-compound, we may subject it to oxidation: the particular phthalic acid formed indicates the relative positions of the two methyl groups in the hydrocarbon, *provided we know the relative positions of the carboxyl groups in the phthalic acids.*

(2) **Korner's Absolute Method.** In Korner's absolute method of orientation the positions of the substituents is determined *without* the aid of other compounds with substituents in known positions. The method is based on the fact that if a disubstitution product of benzene be converted into a triderivative by further replacement of nuclear hydrogen, the para-compound would give only one trisubstitution product, ortho- would give a mixture of two while the meta- would give a mixture of three. Thus the three dibromobenzenes on further bromination, yield the following trisubstitution products: -

DIBROMO-BENZENES	 ORTHO	 META	PARA
TRIBROMO-BENZENES			

Korner's absolute method may also be employed for the orientation of the tri derivatives, as will be clear from the follwing scheme:

TRIBROMO-BENZENES	 1:2:3	1:2:4	 1:3:5
TETRABROMO-BENZENES			

The main difficulty of the method is that under the practical conditions some of the isomers may be produced in such small proportions as to make their detection impossible. If this difficulty does not arise, the method is ideal.

3. Directive Influence Substituents. A substituent already present in the benzene ring exerts an influence on the position taken up by a second substituent entering the ring. There are two distinct types of substitution : either the ortho-compound and the para-compound predominate (**orthopara-substitution**) or the meta-compound constitutes the chief product (**meta-substitution**). The groups thatpossess the *ortho-para directive influence* are :—

$$—Cl, —Br, —I, —OH, —NH_2, —CH_3 ;$$

and those that possess the *meta directive influence* are :—

$$—NO_2, —SO_2OH, —CN, —CHO, —COOH, CH_3CO—$$

Crum Brown and Gibson's rule states that if the substituent, X already present in the nucleus forms with hydrogen a compound, HX, which can be *directly* oxidized to the corresponding hydroxy compond, XOH, the new entrant will take up the *meta*-position. Otherwise it will take up ortho- and the para-positions.

QUESTIONS

1. What do you understand by "position isomerism" in the aromatic series ? Discuss Korner's absolute method of orientation. (*Punjab, Inter., 1932 1918*)

2, Three isomeric chlorotoluenes are known. How would you proceed to determine the position of chlorine in relation to methyl group ? (*Punjab, Inter., 1931*)

3. What is Crum Brown and Gibson's rule for the position taken up by a second group when substituted in a benzene ring which has already been substituted ? (*Punjab, Inter., 1918 ; 1927 ; 1928*)

4. Explain what is meant by orientating influence. What is the orientating influence exerted by each of the following groups when present in an aromatic compound ?—(*a*) NH_2 (*b*) OH, (*c*) NO_2 and (*d*) CHO (*Punjab, Inter., 1933*)

5. What directive influence does one substituent in a benzene ring exert ou a new entraut ? Hence predict, giving arguments the position that a new substituent will take up when each one of the following groups are separately present in the benzene ring :—(*a*)—OH, (*b*)—NO_2, (*c*)—NH_2, (*d*)—COOH, (*e*)—Br, (*f*)—CH_3. (*East Punjab, Inter., 1948*)

CHAPTER 27

HOMOLOGUES OF BENZENE

1. Alkyl Benzenes. The homologues of benzene are derived from benz-ne by the substitution of one or more atoms of hydrogen by alkyl groups. Th egeneral formula of this homologous series is CNH_{2n-6}. Toluene or methylbenzene, $C_6H_5CH_3$, is the simplest of the alkyl derivatives of benzene.

The molecule of an alkyl benzene consists of two parts : the alkyl group, called the **side-chain**, and the benzene residue, called the nucleus. Substitution of the hydrogen atoms of the nucleus and those of the side-chain gives rise to compounds possessing very different properties.

2 General Methods of formation. The general methods for the preparation of the homologues of benzene may be divided into two classes : (*a*) the methods based on the *introduction of an alkyl group into the benzene nucleus* and (*b*) those based on the *removal of a substituent already present in the benzene nucleus* i.e., replacing it by a hydrogen atom.

(a) Introduction of an Alkyl Group into Benzene Nucleus :

(1) Friedel and Crafts' Reaction. When an aromatic hydrocarbon is treated with an alkyl halide in the presence of anhydrous aluminium chloride, one or more of the hydrogen atoms of the nucleus are replaced by alkyl groups :

$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5.CH_3} + HCl$$

$$C_6H_6 + 2CH_3Cl \xrightarrow{AlCl_3} \underset{\text{Xylene}}{C_6H_4(CH_3)_2} + 2HCl$$

Dry benzene, or one of its homologues, together with about one-third its weight of anhydrous aluminium chloride, is placed in a well-dried round-bottom flask fitted with a reflux condenser, and the alkyl chloride or bromide is passed into the mixture, if a gas, or dropped in, if a liquid (Fig. 1). The flask is then heated on a water-bath, until the evolution of HCl or HBr is over. When the product is quite cold, water is added to it gradually, in order to dissolve aluminium chloride. The oily layer of hydrocarbons is separated, dried with calcium chloride, and then fractionated.

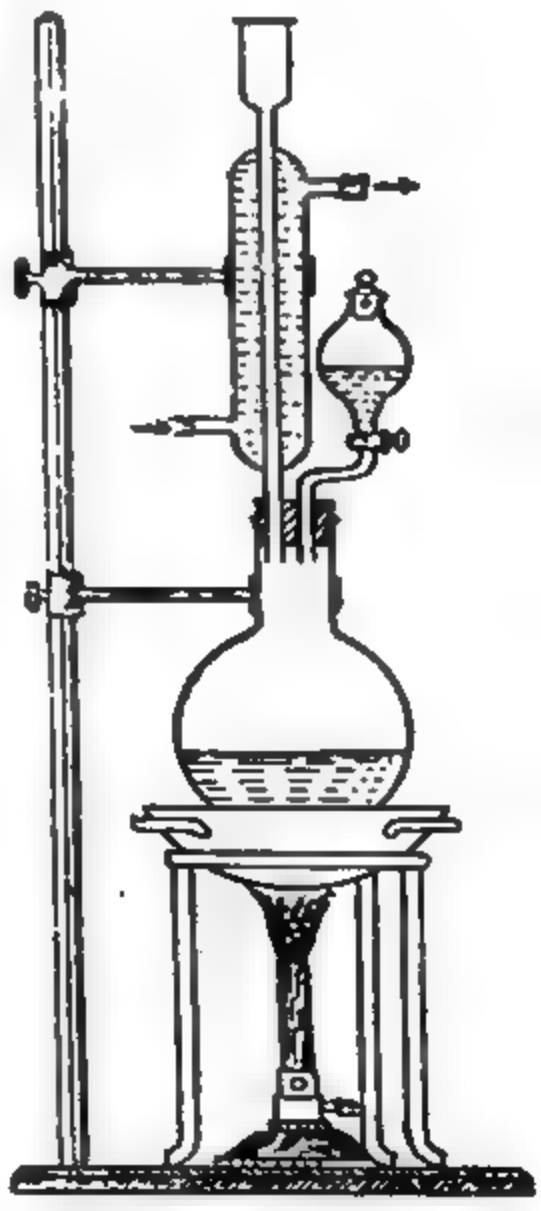


Fig. 1.

(2) Fittig's Reaction. In this method a halogen derivative of a benzene hydrocarbon is heated with an alkyl halide and metallic sodium in the presence of dry ether: *e.g.*,

$$\underset{\substack{\text{Bromo-}\\\text{benzene}}}{C_6H_5Br} + \underset{\substack{\text{Ethyl}\\\text{iodide}}}{C_2H_5I} + 2Na \rightarrow \underset{\substack{\text{Ethyl-}\\\text{benzene}}}{C_6H_5.C_2H_5} + NaBr + NaI$$

(b) Removal of a Substituent present in Benzene Nucleus :

(1) *From an Aromatic Acid.* When an aromatic acid, or its sodium salt, is heated with soda-lime, the carboxyl group is removed and a benzene hydrocarbon results:

$$\underset{\text{Toluic acid}}{C_6H_4(CH_3).COOH} + CaO \rightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + CaCO_3.$$

(2) *From an Aromatic Sulphonic Acid.* An aromatic sulphonic acid, when heated strongly with concentrated hydrochloric acid in a sealed tube, is hydrolysed to give the corresponding hydrocarbon :—

$$\underset{\text{Toluene sulphonic acid}}{C_6H_4(CH_3)\,SO_2.OH + H.OH} \rightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + \underset{\text{Sulphuric acid}}{SO_2(OH)_2}$$

(3) *From a Phenol.* When the vapour of a phenol is passed over strongly heated zinc dust, the oxygen of the hydroxyl group is eliminated, with the production of a benzene hydrocarbon :—

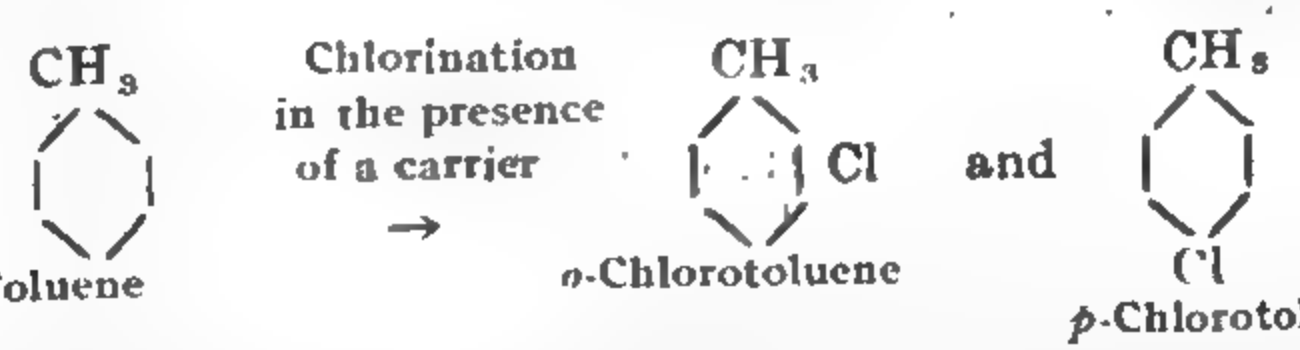
$$\underset{\text{Cresol}}{C_6H_4(CH_3)OH} + Zn \rightarrow \underset{\text{Toluene}}{C_6H_5\,CH_3} + ZnO.$$

(4) *From a Diazonium Salt.* When a solution of a diazonium salt is heated with alkaline stannous chloride, the diazonium group is replaced by hydrogen, and a benzene hydrocarbon results :

$$\underset{\text{Toluene-diazonium chloride}}{C_6H_4(CH_3)N_2Cl} + 2H \rightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + N_2 + HCl.$$

3. Physical Properties. The homologues of benzene are generally colourless, oily liquids with an aromatic, benzenelike odour. Like benzene, they are insoluble in water, but soluble in all proportions in alcohol ether and petroleum.

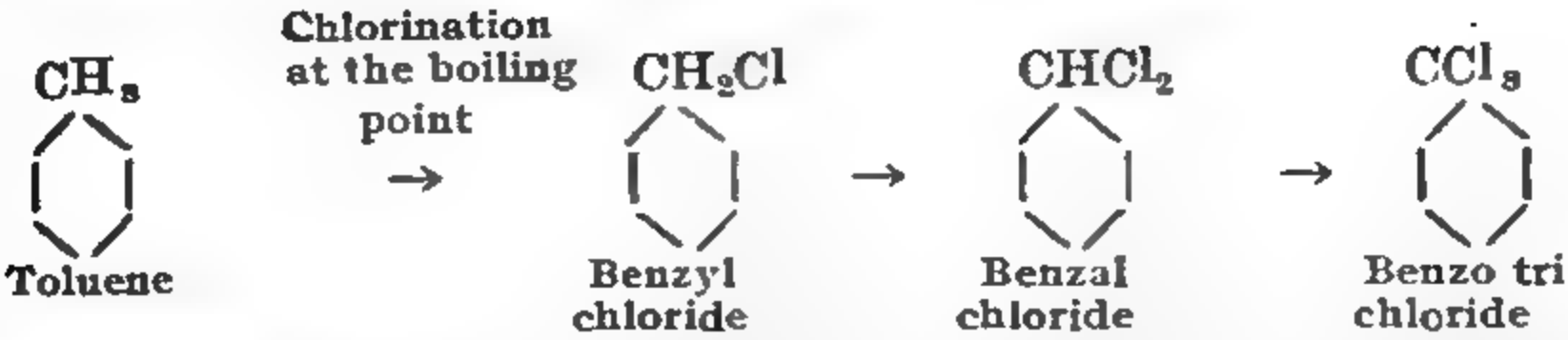
4. Chemical Properties. In their chemical behaviour, the alkyl derivatives of benzene possess a dual character. Firstly, they show all the characteristics of the benzene nucleus *i.e.*, they undergo **nitration, sulphonation, halogenation,** *etc*, forming nuclear substitution products, in exactly the same way as benzene itself (*see p.* 233-234). Secondly, by virtue of the side-chain present in the molecule, they also possess certain aliphatic characters. Thus, toluene, on treatment with chlorine, yields two kinds of products. When chlorine is passed into cold toluene, in the presence of a halogen-carrier (iron filings, aluminium powder, iodine, etc.), substitution occurs in the nucleus (compare benzene, *p.* 234), and a mixture of *p* and o-chlorotoluenes[1] produced:—



Toluene — *o*-Chlorotoluene — *p*-Chlorotoluene

If, on the other hand, chlorine be passed into boiling toluene, preferably in direct sunlight, substitution occurs in the side-chain, the three hydrogen atoms of methyl group being successively replaced by chlorine atoms (compare methane) :—

[1] This is in accordance with the Crum Brown-Gibson rule (Sec. 224).



A characteristic property of alkyl benzenes is their **behaviour on oxidation.** When treated with dilute nitric acid, chromic acid or potassium permanganate, the side-chain, no matter how many carbon atoms it contains, is oxidized to carboxyl group : *e.g.*,

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 3O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5.COOH} + 2H_2O$$

$$\underset{\text{Ethyl benzene}}{C_6H_5.CH_2.CH_3} + 6O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5.COOH} + CO_2 + 2H_2O.$$

If the hydrocarbon contains two or more side-chains, *each* one of these is oxidized to carboxyl ; *e.g.*,

$$\underset{\text{Xylene}}{C_6H_4(CH_3)_2} + 6O \rightarrow \underset{\text{Phthalic acid}}{C_6H_4(COOH)_2} + 2H_2O.$$

The reaction may, therefore, be used to determine the number of side-chains present in the molecule of a benzene homologue, by finding the basicity of the resulting acid. It may also be employed for determining the relative positions of the side-chains in the ring (compare Chap. 26, Sec. 1). Another use of this reaction is in coverting toluene (or any of its homologues) into benzene, as shown below :—

$$\underset{\text{Toluene}}{C_6H_5.CH_3} \xrightarrow{O} \underset{\text{Benzoic acid}}{C_6H_5.COOH} \xrightarrow{Na_2O_3} \underset{\text{Sodium benzoate}}{C_6H_5.COONa} \xrightarrow[\text{Soda-lime}]{\text{Distil with}} \underset{\text{Benzene}}{C_6H_6}$$

5. Toluene, *Methyl-benzene*, or *Phenylmethane*, $C_6H_5.CH_3$.

Occurrence. Toluene is present in coal-tar. It also occurs among the products of destructive distillation of **Tolubalsam,** hence the name "toluene" given to it by Berzelius.

Preparation. Toluene may be prepared in the laboratory by any of the general methods already described. On a commercial scale, it is isolated from coal-tar (Chap. 25, Sec. 4).

Properties. Toluene, like benzene, is a colourless, highly refracting, mobile liquid with a characteristic aromatic odour. It boils at 110°, and freezes at—98°.

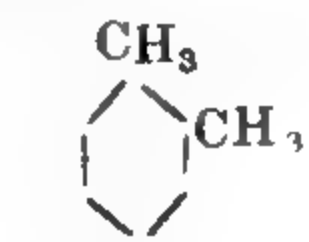
In its chemical properties, toluene resembles other alkyl benzenes (Sec. 4). The action of chlorine on toluene under various conditions has already been described (Sec. 4). When nitrated, toluene, yields chiefly the *o*- and *p*-nitrotoluenes, together with a much smaller proportion of the *m*-compound,

Uses. (1) Toluene is largely employed in the preparation of a large variety of aromatic derivatives, *e.g.*, benzyl chloride, benzal chloride, benzotrichloride, benzaldehyde, benzoic acid, trinitro-toluene, (T.N.T.), etc.

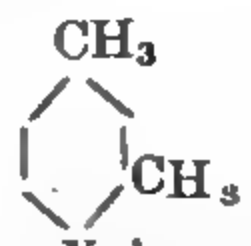
(2) It is also employed as a solvent for phosgene and in dry cleaning.

6. Other Homologues. There are four benzene hydrocarbons

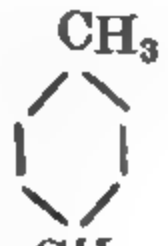
having the formula C_8H_{10}, three dimethylbenzenes or xylenes and one ethylbenzene.



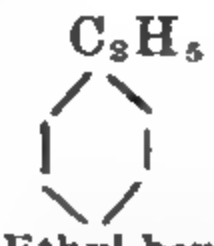
o-Xylene
(b.p. 142°)



m-Xylene
(b p. 139°)

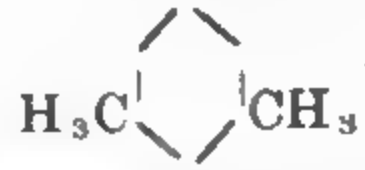


p-Xylene
(b.p. 138°)



Ethyl benzene

The first three occur in coal-tar, *m*-xylene being present in the largest proportion. They may be separated from the coal-tar by the fractionation of 'light oil' They may also be obtained synthetically by the general methods described in Sec. 2.

Mesitylene,  *1*: *3*: *5*- or *s-trimethylbenzene*, is the most

important of the C_9H_{12} hydrocarbons. It occurs to a small extent in coal-tar, but is best obtained by distilling a mixture of acetone (2 vols) concentrated sulphuric acid (2 vols.), and water (1 vol.), a little sand being added to prevent frothing (for equation *see* page 130).

QUESTIONS

1. Give the general methods for the preparation of homologues of benzene. Discuss the action of oxidizing agents on these hydrocarbons. (*Punjab, Inter., 1929*)

2. Describe the physical and chemical properties of alkyl benzenes. How will you determine the relative position of the side-chains in a di-alkyl benzene?

3. How is toluene obtained? Compare its properties with those of benzene. (*Punjab, Inter., 1925*)

4. Write the structural formulae of three different homologues of benzene. What are the general chemical characteristics of aromatic hydrocarbons?

5. How would you prepare toluene from benzene and benzene from toluene? (*Bombay, Inter., 1940*)

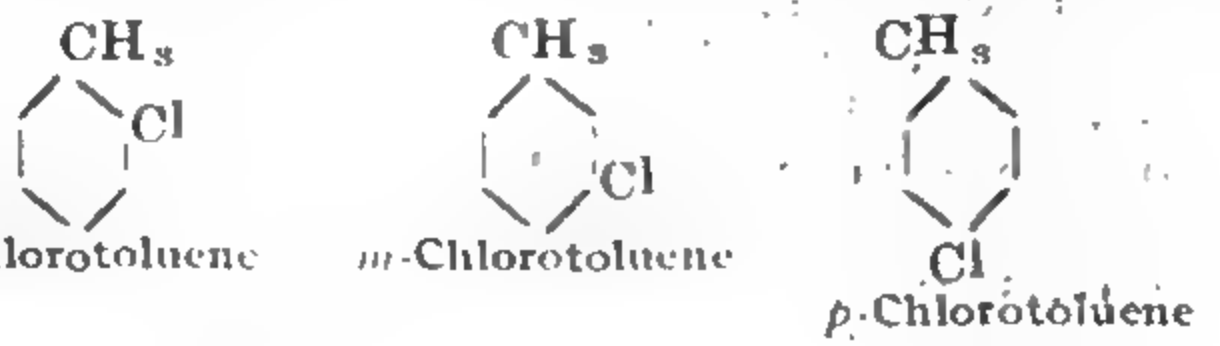
6. Describe the preparation and properties of toluene. How is it converted into its commercially important derivatives? (*Punjab, Inter., 1942*)

CHAPTER 28

AROMATIC HALOGEN COMPOUNDS

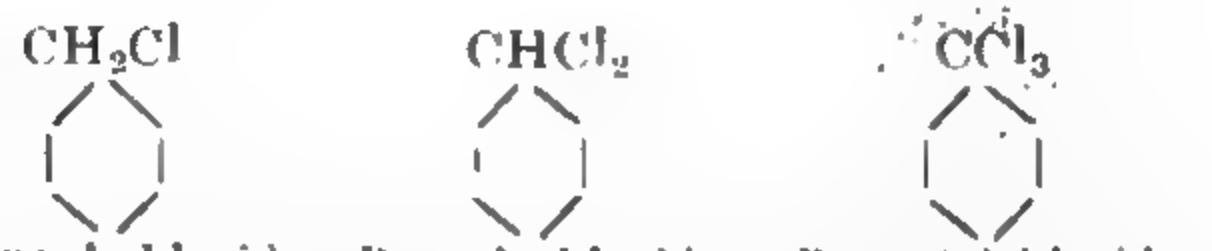
1. General. The halogen substitution products of the aromatic hydrocarbons (in common with all other classes of aromatic derivatives) are divided into **twogroups** : (1) the derivatives which have the halogen atom directly linked to the carbon of the nucleus, and (2) those in which the substituent is present in the side-chain. Benzene, since it contains no side-chain, forms only the derivative of the first kind, *e.g.*, chlorobenzene, C_6H_5Cl, bromobenzene C_6H_5Br, etc. Toluene, in common with other alkyl benzenes, forms derivatives of both kinds ; *e.g.*,

Class I :



o-Chlorotoluene *m*-Chlorotoluene *p*-Chlorotoluene

Class II :



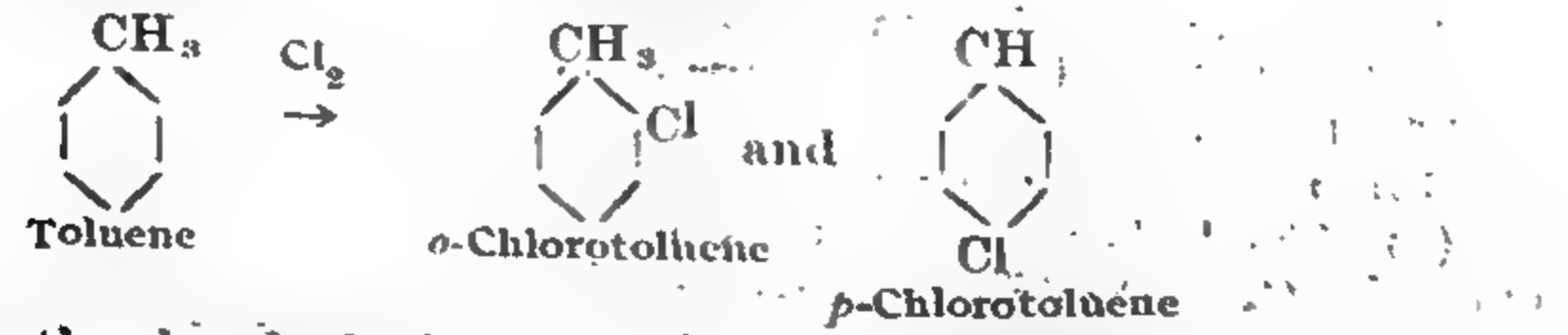
Benzyl chloride Benzal chloride Benzotrichloride

The two classes of derivatives differ from one another both in their methods of preparation and properties. The members of the second group, *i.e.*, those containing the halogen in the side-chain, are, as a rule, very similar to the halogen derivatives of the aliphatic hydrocarbons.

2. Methods of Preparation. The following general methods are employed for the preparation of halogen derivatives of aromatic hydrocarbons :

(1) *By the direct Action of the Halogen.* **Aromatic chloro- and bromo-derivatives** may be obtained by the direct chlorination or bromination of benzene and its homologues. When chlorine or bromine is added to an aromatic hydrocarbon at the ordinary temperature, in the presence of a halogen carrier (iron, aluminium, or iodine), the hydrogen of the nucleus is replaced by the halogen. Thus :

Benzene Bromobenzene



Toluene *o*-Chlorotoluene *p*-Chlorotoluene

If, on the other hand, the halogen is added to a homologue of benzene at its boiling point, preferably in direct sunlight, substitution occurs

in the side-chain. Thus, toluene with chlorine gives benzyl chloride, $C_6H_5.CH_2Cl$, benzal chloride, $C_6H_5CHCl_2$, and benzotrichloride, $C_6H_5CCl_3$ (Sec. 4).

The **iodo-derivatives** of benzene hydrocarbons *cannot* be obtained by the action of the halogen alone, because of the strongly reducing action of hydrogen iodide on the iododerivative first produced. Hence, the hydrocarbon is heated with iodine and an *oxidizing agent*, such as iodic acid or mercuric oxide, which oxidizes the hydriodic acid to iodine, and thus enables the reversible reaction

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI$$

to proceed to completion.

(2) **Sandmeyer's Reaction.** A very important general method for preparing aromatic halogen derivatives, containing the halogen in the *nuclues*, consists in decomposing the solution of a diazonium salt. To obtain a chloro- or a bromo-derivative, the solution of the dizonium salt is warmed with a solution of cuprous chloride in hydrochloric acid or a solution of cuprous bromide in hydrobromic acid ; the cuprous salt here simply acting as a catalyser :

$$\underset{\text{Benzene-diazonium chloride}}{C_6H_5.N_2Cl} \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2$$

$$\underset{\text{Benzene-diazonium chloride}}{C_6H_5.N_2Cl} + HBr \rightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2 + HCl$$

For preparing the iodo-derivatives no cuprous salt need be used as the catalyst ; the reaction proceeds rapidly when the solution containing the diazonium salt is warmed with potassium iodide :

$$C_6H_5N_2Cl + KI \rightarrow C_6H_5I + N_2 + KCl$$

(3) *By the Action of* PCl_5 *on Hydroxy Derivatives.* Aromatic chloro-derivatives are sometimes obtained by treating hydroxy compounds with phosphorus pentachloride :—

$$\underset{\text{Phenol}}{C_6H_5.OH} + PCl_5 \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5.CH_2OH} + PCl_5 \rightarrow \underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} + POCl_3 + HCl$$

3. Physical Properties. The aromatic halogen derivatives are liquids or solids of comparatively high boiling point. They are all insoluble in water, but soluble in alcohol and ether. The derivatives in which the halogen is linked directly to the carbon of the ring have rather a pleasant aromatic odour, while those containing the halogen in the side-chain possess an extremely irritating odour.

4. Reactions. (1) The halogen in *direct* union with the aromatic ring is, as a rule, very firmly combined and cannot be replaced by the hydroxyl or the amino group by treatment with aqueous alkalies or alcoholic ammonia. Moreover, these compounds cannot be converted into less saturated derivatives by treatment with alcoholic potash.

The halogen atom may, however, be replaced by an alkyl group (*see* **Fitting's reaction**, page 239).

(2) The halogen atom, when present in the side chain, as in benzyl chloride, $C_6H_5CH_2Cl$, is readily replaceable. Thus :—

$$\underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} + KOH \rightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + KCl$$

$$\underset{\text{Benzyl chloride.}}{C_6H_5.CH_2Cl} + NH_3 \rightarrow \underset{\text{Benzylamine}}{C_6H_5.CH_2\,NH_2} + HCl$$

(3) Both classes of aromatic halogen derivatives resemble alkyl halides in forming **Grignard's reagents**, when treated in dry ethereal solution with dry metallic magnesium; *eg.*,

$$\underset{\text{Phenyl bromide}}{C_6H_5Br} + Mg \rightarrow \underset{\text{Phenyl magnesium bromide}}{C_6H_5.Mg.\,Br}$$

$$\underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} + Mg \rightarrow \underset{\text{Benzyl magnesium chloride}}{C_6H_5.CH_2\,Mg.Cl}$$

This fact is of great practical importance, for these compounds, like the aliphatic organo-magnesium halides, find extensive application in synthesizing various classes of derivatives.

5. Distinction between Aromatic and Aliphatic Halogen Derivatives. The aromatic halogen compounds having the **halogen directly attached to the nucleus** *differ* from their aliphatic analogues in the *stability* of the halogen atom. Thus, chlorobenzene, C_6H_5Cl. does *not* react with aqueous alkalies, alcoholic ammonia etc. The aliphatic halogen compounds, on the other hand, readily react with aqueous alkalies, alcoholic ammonia and many other reagents, so that the halogen atom gets replaced by various substituents (see Sec. 5, p. 80)

On the other hand, the aromatic halogen derivatives containing the **halogen in the side chain** closely *resemble* the aliphatic halogen compounds. The halogen atom in these is as readily replaced by various substituents as in the case of alkyl halides.

6. Chlorobenzene, Phenyl Chloride, C_6H_5Cl, or

Preparation. Chlorobenzene may be obtained by any of the general methods already described. It is most conveniently prepared by the **Sandmeyer's reaction**. (Chap. 20, Sec. 9).

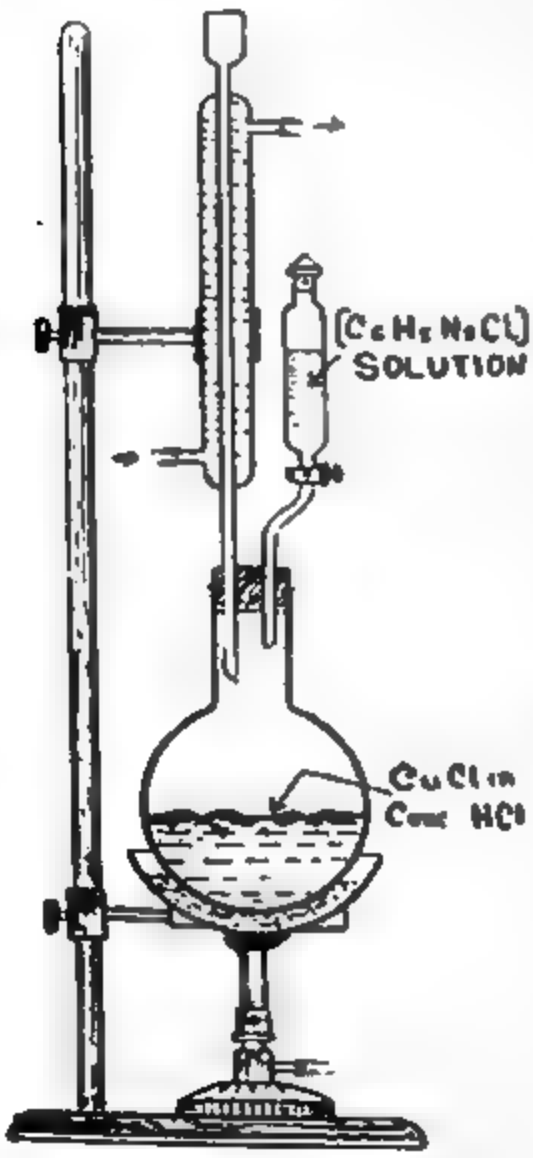


Fig. 1. Preparation of Chlorobenzene.

Aniline (1 part) is diazotized by means of sodium nitrite and concentrated hydrochloric acid (Chapter 31). The resulting cold solution of benzene diazonium chloride is gradually added from a top-funnel into a boiling solution of cuprous chloride (½ part) in concentrated hydrochloric acid (5 parts) contained in a round-bottom flask fitted with a reflux condenser (Fig. 1). When the evolution of nitrogen has ceased, the chlorobenzene is separated by steam distillation, washed, dried and distilled.

On a **commercial scale** chlorobenzene is prepared by the chlorination of benzene. The reaction is carried out in an iron[1] vessel surrounded by a water-jacket for cooling. The vessel is provided with an earthenware pipe through which the hydrogen chloride, evolved during the reaction, escapes. The product is washed with aqueous sodium hydroxide, dried and fractionally distilled to separate chlorobenzene from unchanged benzene and *o*- and *p*- dichlorobenzenes formed simultaneously.

[1] Iron acts as the catalyst. The chlorine being 'dry', does not attack the vessel.

Properties. Chlorobenzene is a colourless, mobile liquid having a pleasant odour and boiling at 132°. It shows the typical behaviour of a halogen derivative substituted in the nucleus, and does not react with aqueous alkalies, ammonia, silver acetate, etc.

Uses. Chlorobenzene is used—
(*i*) as a dyestuff intermediate, and
(*ii*) as an insecticide.

7. Bromobenzene, C_6H_5Br, or

Preparation. (1) Bromobenzene may be prepared from benzene diazonium chloride by the **Sandmeyer's reaction,** using a solution of cuprous bromide in hydrobromic acid.

(2) It is usually prepared by the direct bromination of benzene in the presence of metallic iron or aluminium-mercury couple[1].

Dry benzene (1 part) and aluminium-mercury couple (one hundredth part) is placed in a flask provided with a reflux condenser, to which is attached a tap-funnel and a bent tube for leading off hydrogen bromide into water contained in a beaker (*see* Fig. 2). Dry bromine[2] (2 parts) is gradually dropped in from the tap-funnel. When the mixture has cooled, it is washed successively with dilute sodium hydroxide solution and water, dried and finally fractionated, the fraction passing between 140° and 170° being collected separately.

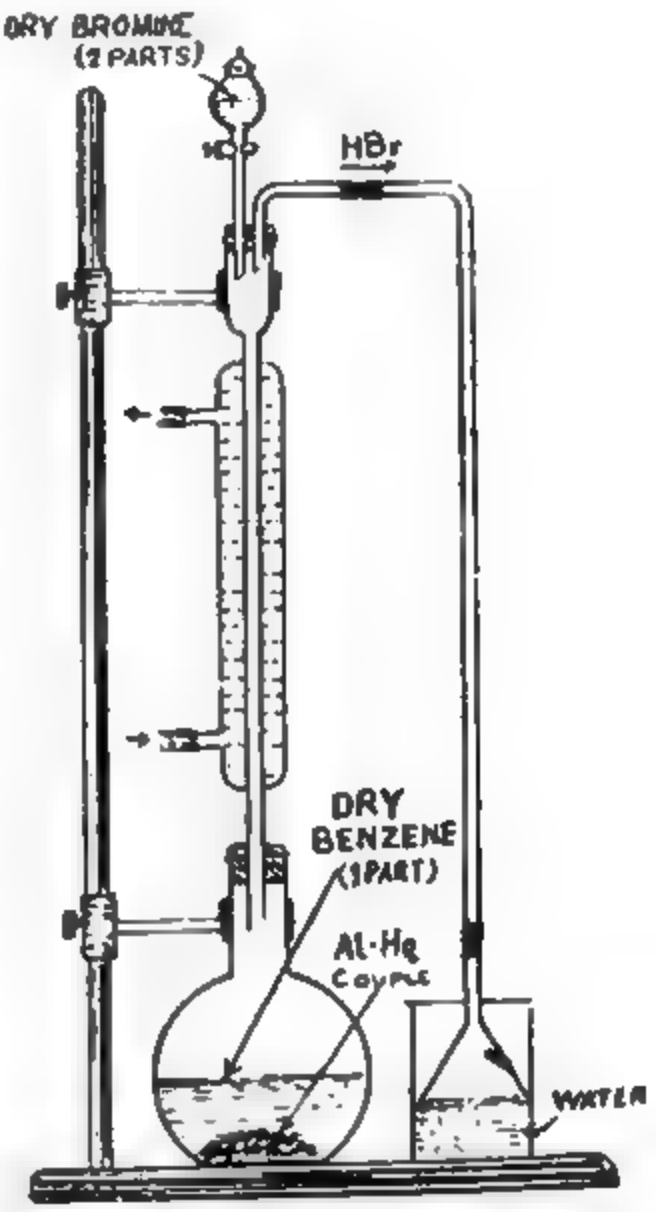


Fig. 2. Bromination of Benzene.

Properties. Bromobenzene closely resembles chlorobenzene in physical and chemical properties. It boils at 155°

8 Idobenzene. *Phenyl Iodide* C_6H_5I.

Preparation. (1) Iodobenezene may be obtained by heating benzene with idoine and iodic acid (*p.* 214).

(2) It is most conveniently prepared by decomposing benzene diazonium sulphate with aqueous potassium iodide,

$$C_6H_5.N_2SO_4H + KI \rightarrow C_6H_5I + N_2 + KHSO_4.$$

Benzene-diazonium sulphate

Aniline (1 part) is diazotized by means of sodium nitrite and dilute sulphuric acid (*p.* 334). The resulting cold solution of benzene diazonium sulphate is added to a concentrated solution of potassium iodide (2 parts), and the mixture is heated on a water-bath, until the evolution of nitrogen has ceased. The liquid is submitted to steam distillation to separate iodobenzene, which is then washed with dilute sodium hydroxide, dried, and distilled.

Properties Iodobenzene is a heavy, colourless liquid. It boils at 188°C.

1. This is prepared by allowing small rolls of aluminium foil to stand in a strong solution of mercuric chloride for about one minute, then removing them from the solution and washing them successively with water, alcohol and benzene.

2. Bromine is dried by shaking it with an equal volume of concentrated sulphuric acid in tap funnel, allowing to stand, and then running off the lower layer of bromine.

9. Benzyl Chloride, $C_6H_5CH_2Cl$, or Benzyl chloride is typical example of a halogen aromatic derivative containing the halogen atom in the *side-chain*.

Preparation. Benzyl chloride may be obtained from benzyl alcohol, $C_6H_5.CH_2OH$, by treatment with phosphorus pentachloride, but is always prepared by passing chlorine through boiling toluene.

Physical Properties. It is a colourless liquid (b. p. 178°) with an unpleasant smell, and has a powerful irritating effect on the eyes and nose.

Reactions. (1) *Nitration.* Like other aromatic derivatives, benzyl chloride can be readily nitrated, and gives a mixture of isomeric nitro-compounds, $C_6H_4(NO_2)\,CH_2Cl$.

(2) *Replacement of the Halogen Atom.* With boiling water, benzyl chloride yields benzyl alcohol.

$$C_6H_5.CH_2Cl + H.OH \rightarrow \underset{\text{Benzyl alcohol}}{C_6H_5\,CH_2OH} + HCl,$$

with alcoholic ammonia, benzylmine.

$$C_6H_5.CH_2Cl + NH_3 \rightarrow \underset{\text{Benzylamine}}{C_6H_5.CH_2NH_2} + HCl.$$

and with silver acetate, benzyl acetate,

$$C_6H_5.CH_2\,Cl + CH_3COOAg \rightarrow \underset{\text{Benzyl acetate}}{CH_3COO.CH_2.C_6H_5} + AgCl.$$

(3) *Oxidation.* The behaviour of benzyl chloride towards oxidizing agents is of great practical importance. When heated with 60 per cent. nitric acid, it yields *benzoic acid*,

$$C_6H_5.CH_2Cl + H.OH \rightarrow C_6H_5.CH_2OH + HCl$$
$$2HNO_3 \rightarrow H_2O + N_2O_3 + 2O$$
$$C_6H_5.CH_2OH + 2O \rightarrow C_6H_5.COOH + H_2O$$
$$\underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} + 2HNO_3 \rightarrow \underset{\text{Benzoic acid}}{C_6H_5.COOH} + N_2O_3 + H_2O + HCl$$

The reaction is employed on a large scale for the manufacture of this acid.

When benzyl chloride is boiled with an aqueous solution of lead nitrate or cupric nitrate, *benzaldehyde* is obtained :

$$C_6H_5.CH_2Cl + H.OH \rightarrow C_6H_5.CH_2OH + HCl \qquad [\times 2]$$
$$Pb(NO_3)_2 + 2HCl \rightarrow PbCl_2 + 2HNO_3$$
$$2HNO_3 \rightarrow H_2O + N_2O_3 + 2O$$
$$C_6H_5.CH_2OH + O \rightarrow C_6H_5.CHO + H_2O \qquad [\times 2]$$
$$2C_6H_5.CH_2Cl + Pb(NO_3)_2 \rightarrow \underset{\text{Benzaldehyde}}{2C_6H_5CHO} + PbCl_2 + N_2O_3 + H_2O.$$

This reaction is employed for the preparation of benzaldehyde in the laboratory and on a commercial scale.

Uses. As already mentioned, benzyl chloride is employed in the manufacture of benzoic acid and benzaldehyde.

10. Banzel Chloride, or *benzylidene chloride*, $C_6H_5.CHCl_2$, (b p. 207°) and **benzene-trichloride,** $C_6H_5.CCl_3$, (b. p. 213°) are both obtained by the prolonged action of chlorine on boiling toluene. They may be separated from the mixture by fractional distillation.

Uses. Benzal chloride and benzotrichloride are both employed industrially, the former in the preparation of benzaldehyde and the latter in that of benzoic acid. In practice, the mixture of the two compounds, obtained as above, is heated with milk of lime, without previous separation, when we get benzaldehyde and the calcium salt of benzoic acid :

$$\underset{\text{Benzal chloride}}{C_6H_5.CHCl_2} \xrightarrow{H.OH} \underset{\text{(unstable)}}{C_6H_5.CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

$$\underset{\text{Benzo-trichloride}}{C_6H_5.CCl_3} \xrightarrow{H\ OH} \underset{\text{(unstable)}}{C_6H_5.C(OH)_3} \xrightarrow{-H_2O} \underset{\text{Benzoic-acid}}{C_6H_5COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca}$$

The reaction mixture is submitted to steam distillation, when benzaldehyde passes over. The residual liquid is then treated with hydrochloric acid to precipitate benozic aoid.

QUESTIONS

1. Give an account of the methods used for the preparation of aromatic halogen compounds. In what way do they differ from their aliphatic analogues ? *(Punjab, Inter., 1930)*

2. Into what different groups are the aromatic halogen derivatives divided ? Describe the chief physical and chemical properties of each group. In what important respect do aromatic iodo-compounds containing the halogen in the nucleus differ from the corresponding chloro- and bromo-derivatives ?

3. Give methods of preparation of chlorobenzene and benzyl chloride. Describe both the physical and chemical properties to illustrate their differences. *(Punjab, Inter., 1945)*

4. How will you prepare a sample iodobenzene ? Give the chief chemical properties of this compound.

5. How are benzal chloride and benzotrichloride prepared on a commercial scale ? To what use are they put ?

6. An organic compound, *A*, was found to contain C=52·2, H=3·7, and Cl=44·1 per cent. When submitted to oxidation, it gave an acid, *B*, which, on being distilled with soda-lime, yielded benzene. Deduce the identity of both *A* and *B*.

Ans. (*A*) Benzal chloride $C_6H_5.CHCl_2$: (*B*) Benzoic acid, C_6H_5COOH.

CHAPTER 29

AROMATIC NITRO COMPOUNDS

1. Nitration. As already mentioned a characteristic property of aromatic compounds is the ease with which they may be converted into nitro-compounds :—

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 \rightarrow \underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + H_2O$$

The process known as **nitration,** is of great practical importance. The actual details of nitration depend on the nature of the compound to be nitrated and on the number of nitro-groups to be introduced.

2. General Method of Nitration. (1) The most common method of nitrating an aromatic compound consists in treating it with a mixture of concentrated nitric acid and concentrated sulphuric acid. The latter substance serves to *bind* the water formed during nitration, and thus prevents nitric acid from becoming too dilute. On the reaction being over, the product is diluted with water, when the nitro-compound is precipitated as an oil or an insoluble solid.

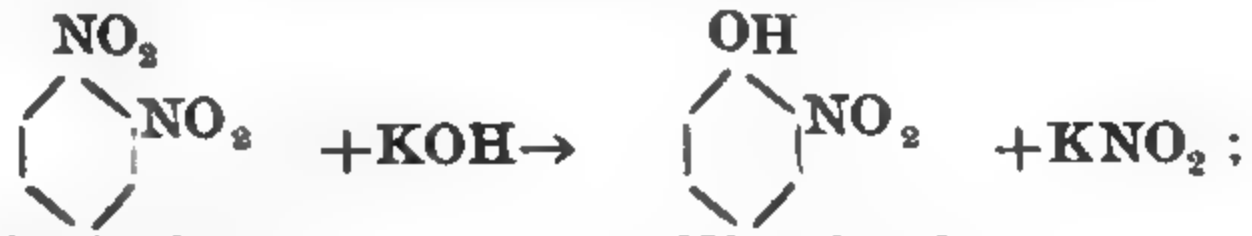
If it is desired to introduce more than one nitro-group in the compound, an excess of a mixture of *fuming* nitric and concentrated sulphuric acid is employed.

(2) A mixture of concentrated nitric acid and acetic anhydride is a very energetic nitrating agent, and gives a better yield of the nitro-compound. The acetic anhydride, like sulphuric acid, serves to bind the water formed in the reaction.

(3) A recent method for nitrating an aromatic compound consists in treating it with nitrogen dioxide in the presence of anhydrous aluminium chloride, the latter substance acting as a catalyst.

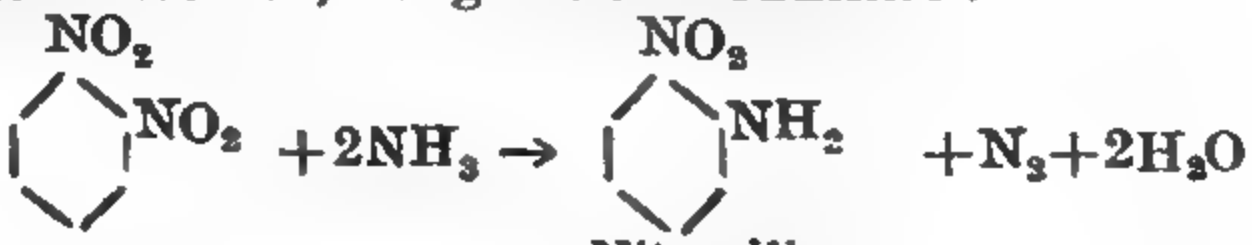
3. Physical Properties. Nitro compounds are oily liquids or crystalline solids, and are usually yellow in colour. They are practically insoluble in water, but readily dissolve in alcohol, ether and other organic solvents. Many of them can be distilled in steam.

4. Reaction. (1) *Replacement of Nitro Group.* In the mono-substituted derivatives, the nitro-group is firmly united to the benzene ring and cannot be directly replaced by other atoms or groups. However, in the case of polynitro derivatives, or halogen-substituted nitro-compounds the nitro group is more or less readily replaceable by other substituents. Thus, ortho-dinitrobenzene, when boiled with aqueous potash, yields ortho-nitrophenol,



o-Dinitrobenzene — *o*-Nitrophenol

with alcoholic ammonia, it gives *o*-nitraniline :—



o-Nitraniline

(2) *Reduction of Nitro-compounds.* This is the most important reaction of nitro-compounds, and is dicussed in the following section.

(3) *Explosive Nature of Polynitro Compounds* Polynitro compounds, such as trinitrobenzene, trinitrotoluene (T N.T,) and trinitrophenol, explode violently when detonated or suddenly heated. The last two compounds are extensively used as explosives.

5. Reduction of Nitro Compounds As already stated, the most important reaction of nitro-compounds is their behaviour on reduction. By carrying out the reduction under different experimental conditions, a variety of products are obtained, as illustrated below in the case of nitrobenzene.

(1) *Reduction in Acid Solution.* When nitrobenzene is reduced in acid solution (*e.g.*, by means of tin and hydrochloric acid), the nitro-group is replaced by the amino-group :—

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \rightarrow \underset{\text{Aminobenzene (aniline)}}{C_6H_5NH_2} + 2H_2O$$

Other nitro-derivatives give rise to the corresponding aminoderivatives.

(2) *Reduction in Neutral Solution.* Reduction of nitro-benzene in neutral solution (*e.g.*, by means of aluminium-mercury couple and water) yields nitrosobenzene and then phenyl-hydroxylamine :

$$C_6H_5NO_2 + 2H \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} + H_2O$$

$$C_6H_5NO + 2H \rightarrow \underset{\text{Phenyl-hydroxylamine}}{C_6H_5.NHOH}$$

(3) *Reduction of Alkaline Solution.* When nitrobenzene is reduced in alkaline solution, a variety of products are obtained. Thus, with sodium and methyl alcohol, we get azoxybenzene :—

$$2C_6H_5NO_2 + 6H \rightarrow \underset{\text{Azoxybenzene}}{\begin{matrix} C_6H_5.N{\rightarrow}O \\ \| \\ C_6H_5.N \end{matrix}} + 3H_2O$$

With stannous chloride and caustic potash, azobenzene is the main product :—

$$2C_6H_5NO_2 + 8H \rightarrow \underset{\text{Azobenzene}}{\begin{matrix} C_6H_5.N \\ \| \\ C_6H_5.N \end{matrix}} + 4H_2O$$

Zinc and caustic soda, acting on nitrobenzene, produce hydrazo-benzene :—

$$2C_6H_5NO_2 + 10H \rightarrow \underset{\text{Hydrazobenzene}}{\begin{matrix} C_6H_5.NH \\ \| \\ C_6H_5.NH \end{matrix}} + 4H_2O$$

The above facts are summarized schematically on page 251.

If any of the reduction products mentioned above be treated with an acid reducing agent, we always get aniline as the final product.

6. Identification of Nitro compounds. The presence of the nitro-group in a compound is indicated by the yellow colour of the substance, which is intensified by alkalies. The test given in the follow-

ing experiment may be employed to confirm the presence of the nitro group.

Expt. 1. *Identification of nitro Compounds* :—

(1) *Reduction to an Amino Compound.* Take about 2 c.c. of concentrated hydrochloric acid in test-tube. Add a drop of a nitrobenzene, and then add zinc-dust in successive, very small amounts, shaking the mixture thoroughly after each addition and keeping it cool under the tap. When the reaction is over, cool the mixture, preferably in ice-cold water, and add a little sodium nitrite solution.

To the resulting solution (which contains a diazonium salt) add a few drops of an alkaline solution of β-napthol. A red precipitate of an **azo dye** is produced.

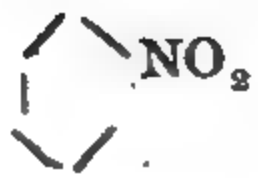
(2) *Reduction to an aryl derivative of hydroxylamine.* Take a few drops of nitrobenzene in a test-tube ; add a few drops of calcium chloride solution and a pinch of zinc-dust. Boil, cool, and filter.

Test the filtrate (which contains **Phenylhydroxylamine,** $C_6H_5NH(OH)$ with Fehling's solution. A red ppt. of cuprous oxide is produced.

$C_6H_5NO_2$

Nitrobenzene

← *Acid reducing agents (e.g., Sn+HCl)*	← Neutral reducing agents (*e.g.*, Al-Hg couple and water)	← Alkaline reducing agents (*e.g.*, $SnCl_2+NaOH$ or $Zn+NaOH$)
$C_6H_5NH_2$ Aniline	C_6H_5NO Nitrosobenzene	$C_6H_5.N\rightarrow O$ ‖ $C_6H_5.N$ Azoxybenzene
	↓	↓
	$C_6H_5N<^{H}_{OH}$ Phenyl-hydroxylamine	$C_6H_5.N$ ‖ $C_6H_5.N$ Azobenzene
		↓
		$C_6H_5.NH$ | $C_6H_5.NH$ Hydrazobenzene

1. Nitrobenzene,  **or** $C_6H_5NO_2$.

Preparation. Nitrobenzene is prepared by heating benzene with a mixture of nitric and sulphuric acids :—

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 \rightarrow \underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + H_2O$$

Expt. 2. *Preparation of Nitrobenzene*: To 50 c.c. of pure benzene placed in a half-litre, round-bottom flask, is added, in small quantities at a time, a well-cooled mixture of concentrated nitric acid (60 c.c) and concentrated sulphuric acid (70 c.c.) After each addition, the contents of the flask must be well shaken, and the flask cooled under the tap. The temperature must, on no account, be allowed to rise above 50°, as this would result in the formation of dinitrobenzene. When all the acid mixture has been added, a vertical air condenser, is attached to the flask ; which is then heated for about an hour by immersion in a water bath kept at 50° to 60°, the flask being well shaken periodically during the heating.

After cooling, the contents of the flask are poured into a separating funnel and the *lower layer of acid* is run off. The oily layer of nitrobenzene is washed once with water, then with dilute sodium carbonate solution, and finally again with water the *lower layer of nitrobenzene* being drawn off each time.

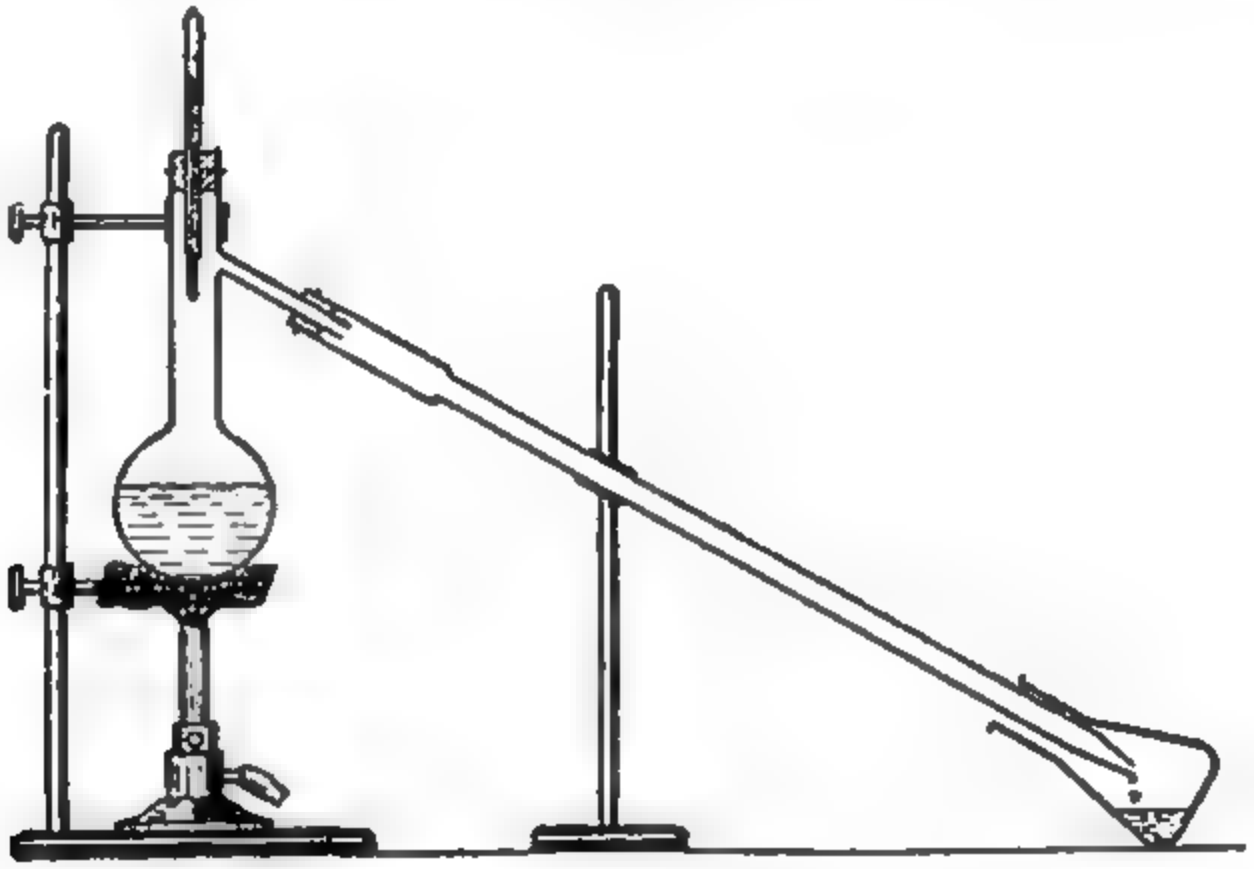


Fig. 1. Distillation of Nitrobenzene.

The nitrobenzene, which is turbid because of its being moist, is then allowed to stand over fused calcium chloride, until it gets clear. It is then distilled from distillation flask, provided with a thermometer and a long air condenser (Fig. 1) the fraction passing at 204° to 207°C. being collected separately. The distillation must not be carried out to dryness as this might lead to an explosion.

Manufacture. The method employed in the manufacture of nitrobenzene is similar to that used in the laboratory. The usual amounts of the reactants used in one operation are :

Benzene, 500 gallons. Nitric acid, 5000 lbs. Sulphuric acid, 6600 lbs.

A sketch of the nitrobenzene plant is given in Fig. 2. The benzene is placed in the cast iron nitrating pan provided with lead cooling coils and a central shaft carrying two spiral agitators, *s,s*. The acid mixture contained in the mixed-acid pan is run in a fine stream, the contents of of the nitrating pan being constantly stirred. The flow of the nitrating acid is so regulated that the temperature does not exceed 60°C. After the whole of the acid mixture has been added, the agitation of the contents of the nitrating pan is continued for 4½ hours.

At the end of this time, the nitration is complete and the contents of the pan are allowed to settle for about 5 hours. The lower layer consisting of dilute sulphuric acid, is run into the air pressure egg,

whence it is blown to a concentrator. The concentration of the acid is usually effected by the cascade system, and the concentrated acid is used overagain.

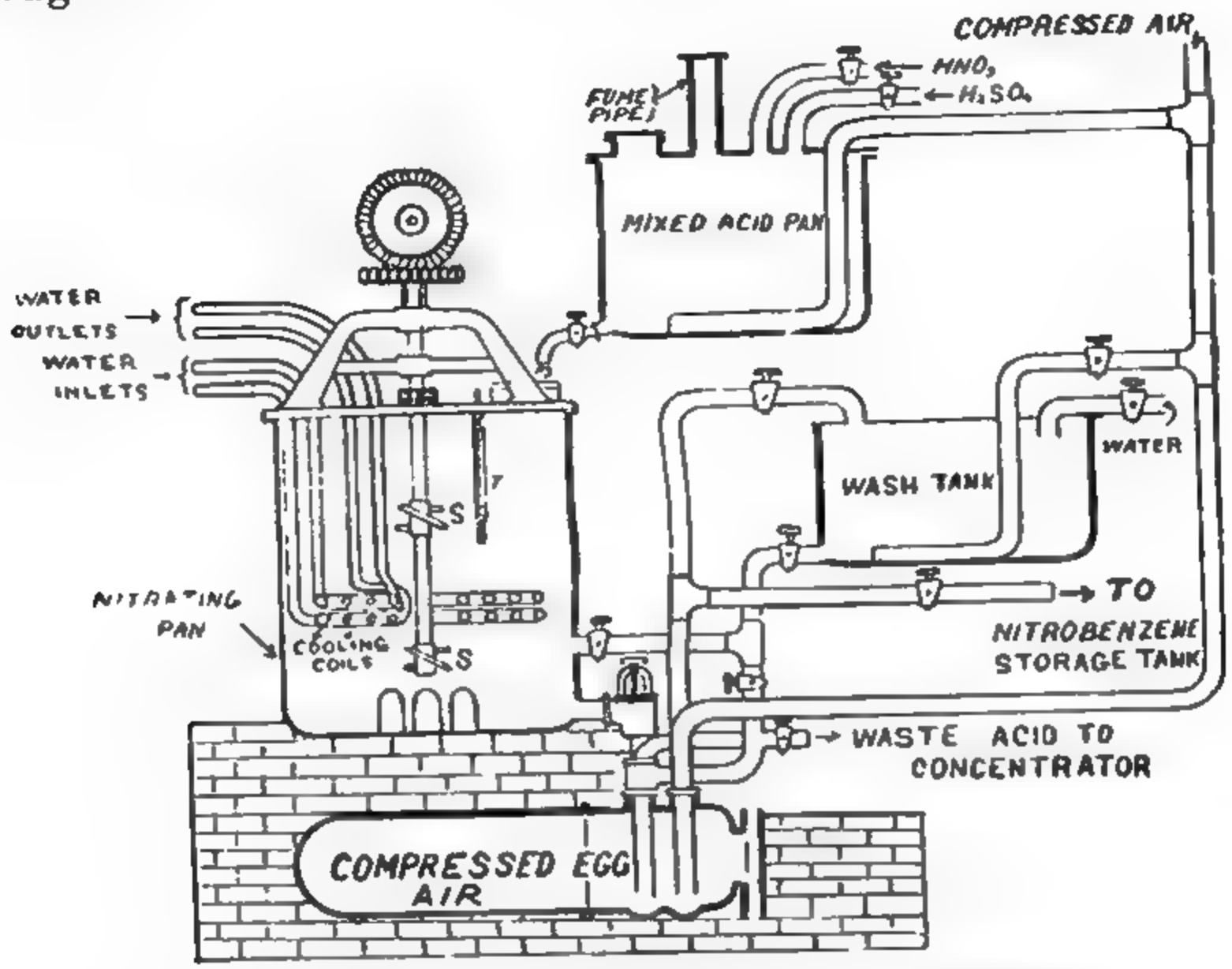


Fig. 2. Plant for the Manufacture of Nitrobenzene

When the waste acid has been forced to the concentrator, the nitrobenzene is run into the egg and thence blown into the washing tank. Hence it is mixed with an equal volume of water (containing a little sodium hydroxide to nextralize any free acid present), and the mixture is well agitated by means of a jet of compressed air. The contents of the washing tank are allowed to settle for several hours. The nitrobenzene, which now forms the lower layer, is run into the egg, and thence blown into storage tanks.

Properties. Nitrobenzene is a pale yellow oil of sp. gr. 1·2 at 20°, and has a strong odour like that of bitter almonds. It is insoluble in water, but readily dissolves in organic solvents. It boils at 208°, and is volatile in steam.

When treated with tin and hydrochloric acid (or iron and water in the presence of a little hydrochloric acid) nitrobenzene is reduced to amino benzene or aniline, $C_6H_5NH_2$:—

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O$$

This reaction is of great commercial importance, since aniline is the starting material in the manufacture of dyes.

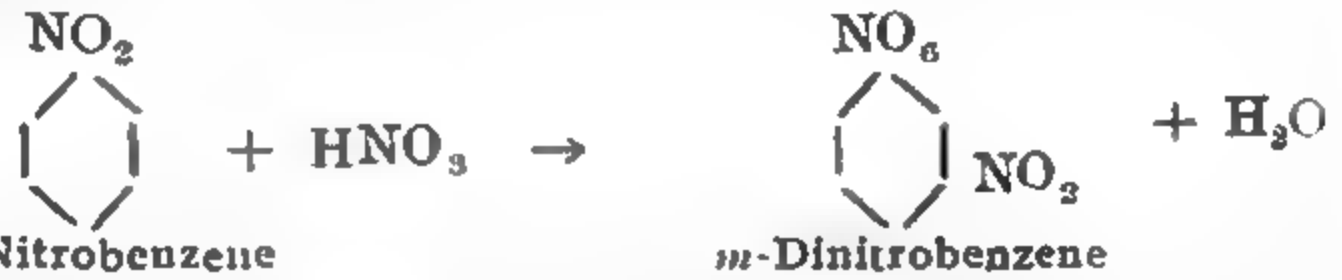
The various products obtained by the reduction of nitrobenzene under different conditions are given on pp. 250, 251. All these substances, when subjected to further reduction by means of tin and hydrochloric acid, yield aniline as the final product.

Uses. (1) The chief use of nitrobenzene is in the manufacture of aniline.

(2) It is also employed, under the name of oil of **mirbane,** in scenting cheap soaps, boot polishes, etc., where a disagreeable odour has to be covered.

8. ***m*-Dinitrobenzene,** or $C_6H_4 < \begin{matrix} NO_2\ (1) \\ NO_2\ (3) \end{matrix}$

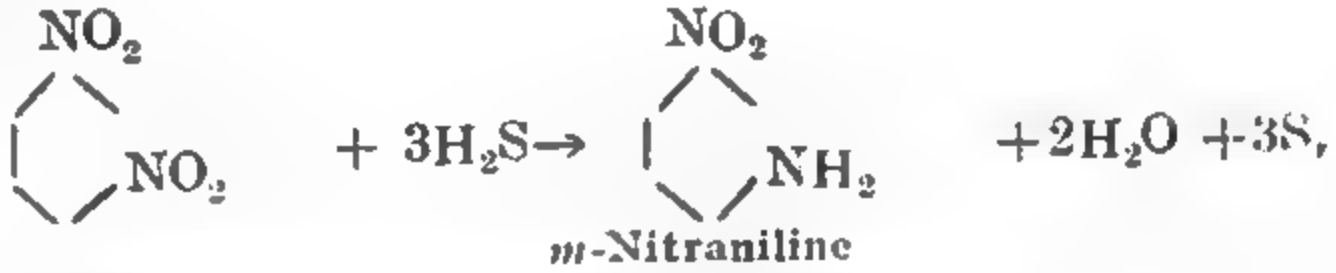
Preparation. *m*-Dinitrobenzene is prepared by the further nitration of nitrobenzene :—



Nitrobenzene *m*-Dinitrobenzene

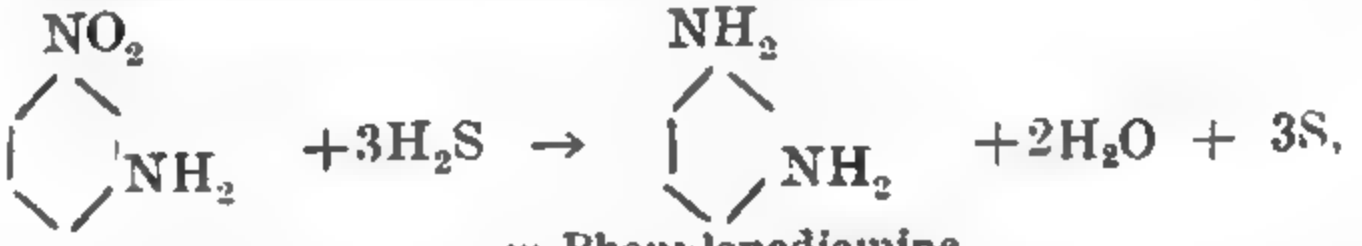
Nitrobenzene (1 part) is added gradually to a mixture of concentrated nitric acid (1½ parts) and concentrated sulphuric acid (3 parts). The reaction mixture is then heated on a sand-bath, until a drop of the oily liquid when stirred with cold water solidifies completely. It is then poured, while still hot, into a large quantity of cold water. The solid *m*-dinitrobenzene that separates out is filtered, washed with cold water, and crystallized from hot alcohol.

Properties. *m*-Dinitrobenzene forms pale-yellow crystals (m. p. 90°) When reduced with alcoholic ammonium sulphide, it is first converted into *m*-nitraniline,



m-Nitraniline

and then into m-**phenylenediamine** (*m*-diaminobenzene).



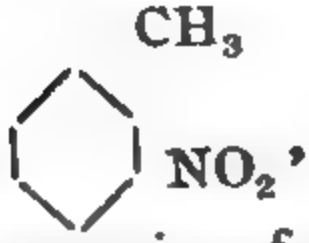
m-Phenylenediamine

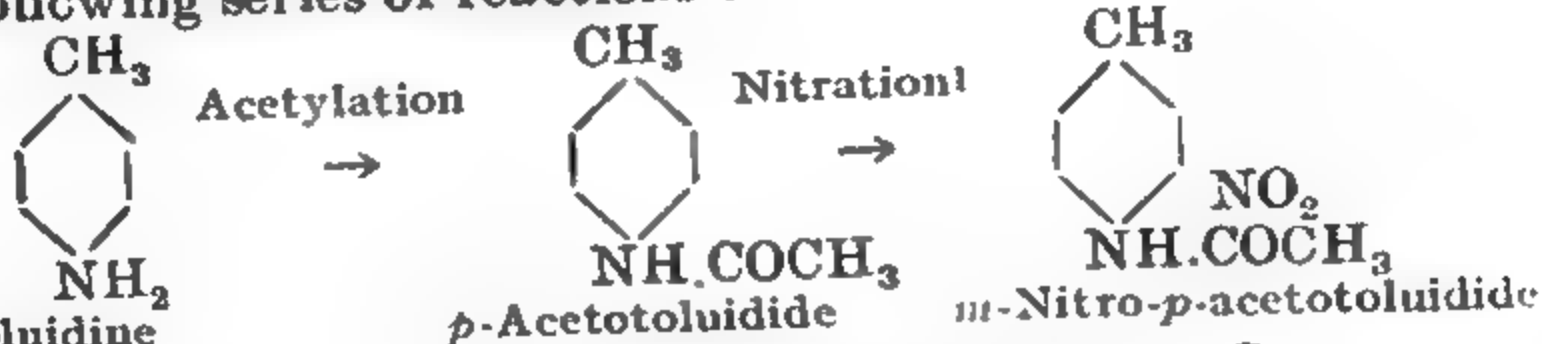
Uses. *m*-Dinitrobenzene is employed for the preparation of *m*-nitraniline and *m*-phenylenediamine, both of which find application in the dye industry. It also enters into the composition of certain explosives.

9. Nitrotoluenes. There exist three mononitrotoluenes, *ortho-meta* and *para*.

O-**Nitrotoluene.** This substance is obtainted, together with *para* compound, by the nitration of totulene, and is separated from the other product by fractional distillation (the boiling points of the two compounds being 218° and 230° respectively). When submitted to oxidation, *o*-nitrotoluene yields *o*-nitobenzaldehyde.

Use. *o*-Nitotoluene is largely used in the manufacture of *o*-toluidine (*i.e.* *ortho*-aminotoluene).

m-**Nitrotoluene,**  , **is best prepared from** *p*-**toluidine through the following series of reactions :—**



It melts at 16° and boils at 230°.

p-**Nitrotoluene,** CH_3 NO_2, **is obtained, along with the** *ortho* **compound by the nitration of toluene. It melts at 53° and boils at 230°. It is used in the manufacture of** *p*-**toluidine and as an intermediate in the manufacture of the dye called Direct Yellow.**

2:4:6-**Trinitroluene** (T.N.T. **is an important explosive, and is prepared in two steps : The mixture of mononitrotoluenes (M.N.T.), produced in the first operation, is subjected to further nitration by means of a mixture of concentrated nitric acid and fuming sulphuric acid, when trinitrotoluene is obtained. It is a pale yellow, crystalline solid melting at 80·8°.**

Trinitrotoluene mixed with 4 times its weight of ammonium nitrate is much used as an explosive under the name "amatol."

QUESTIONS

1. **Describe the various methods that are used in the preparation of nitro-derivatives of aromatic compounds. Give instances of compounds in which the nitro-group may be replaced by other substituents.**

2. (*a*) **State the general methods used for the nitration of aromatic compounds.**
(*b*) **Indicate what happens when nitrobenzene is reduced in—(*i*) Acid solution, (*ii*) neutral solution, (*iii*) alkaline solution.** (*Punjab, Inter., 1940*)

3. **How will you proceed to find the presence of a nitro group in a given aromatic substance ? Give practical details.**

4. **State briefly but exactly the experiment you would perform in the laboratory to prepare a pure specimen of nitrobenzene. What is this compound used for ?** (*Punjab, Inter., 1932*)

5. **How is nitrobenzene prepared on a commercial scale ? Draw a neat sketch of the plant employed, and describe the procedure in detail**

6. **Describe the preparation, chief properties and uses of** *m*-**dinitrobenzene.**

---

[1] **In this reaction the nitro group enters the** *ortho*-**position to the substituted amino group, the para position being already occupied by the methyl group.**

[2] **The diazonium compound first produced is** *reduced* **by alcohol, the diazonium group being thereby replaced by hydrogen.**

CHAPTER 30

AROMATIC AMINO COMPOUNDS

1. The true **aromatic amino-compounds** contain the—NH_2 group in *direct* union with the benzene nucleus, *e.g.*, amino-benzene, $C_6H_5NH_2$, amino-toluenes, $C_6H_4<^{CH_3}_{NH_2}$, etc. When the amino group is present in the side-chain, the compound is termed an **aromatic amine**, *e.g.*, benzylamine, $C_6H_5.CH_2.NH_2$. The former class differ in some important respects from primary aliphatic amines, while the latter class resemble the aliphatica amines closely.

In addition to the above two classes of compounds, there exist purely aromatic, and mixed aliphatic-aromatic, secondary and tertiary amines *e.g.*,

Diphenylamine, $(C_6H_5)_2NH$
Triphenylamine, $(C_6H_5)_3N$
Methylaniline, $C_6H_5.NH.CH_3$
Dimethylaniline, $C_6H_5.N(CH_3)_2$.

2. **Primary Amino-Compounds.** This is the most important group of the aromatic amino compounds. The members of this group contain an—NH_2 group in direct union with the benzene nucleus.

General Methods of Formation :—

(1) *From Nitro-compounds.* The aromatic amino compounds are almost exclusively obtained by the reduction of the corresponding nitro-compounds :—

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \rightarrow \underset{\text{Aminobenzene}}{C_6H_5NH_2} + 2H_2O.$$

The reduction is effected by various means, such as by the use of tin and hydrochloric acid, stannous chloride and hydrochloric acid, iron and hydrochloric acid, alcoholic ammonium sulphide, alcoholic stannous chloride, or electrolytically.

(2) *From Phenols.* Aromatic amino compounds can also be obtained from phenols by heating the latter at 300° with the double compound of zinc chloride and ammonia, $ZnCl_2.NH_3$; *e.g.*,

$$\underset{\text{Phenol}}{C_6H_5OH} + NH_3 \rightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O.$$

(3) *From carboxylic Acid.* The carboxyl group of a carboxylic acid may be replaced by an—NH_2 group by heating the ammonium salt of the acid and submitting the resulting acid amide to Hofmann's bromamide reaction (*p.* 152).

$$\underset{\text{Benzoic acid}}{C_6H_5.COOH} \rightarrow \underset{\text{Benzamide}}{C_6H_5.CO.NH_2} \rightarrow \underset{\text{Aniline}}{C_6H_5.NH_2}$$

Physical Properties. The primary amino-compounds are colourless liquids or solids. They are sparingly soluble in water, are volatile in steam, and can be distilled without decomposition under the atmospheric pressure.

Reaction. Owing to the electronegative character of the benzene nucleus, these compounds possess only a weak basic character. They resemble aliphatic amines in their behaviour towards alkyl

halides, acid chlorides, and chloroform (see *p.* 169). They differ from them in the following respects :—

(1) When treated with nitrous acid in the cold, they give *diazo-compounds*.

(2) They possess the typical aromatic character and the hydrogen of the nucleus can be more readily replaced than in benzene itself.

(3) They are also far susceptible to oxidation than the aromatic hydrocarbons. The above reactions are described in detail under aniline.

3. Aniline. or $C_6H_5.NH_2$.

Aniline, *amino-benzene phenylamine*, is the most important representative of the aromatic amino-compounds containing the—NH_2 group in direct union with the benzene nucleus. The name aniline is derived from the portuguese word *anil* meaning indigo ; the compounds being first obtained by the distillation of this substance.

Preparation. Aniline is prepared in the laboratory by the reduction of nitrobenzene by means of tin and hydrochloric acid :—

$$\underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + 6H \rightarrow \underset{\text{Aniline}}{C_6H_5.NH_2} + 2H_2O$$

Expt. 1. *Preparation of Aniline.* Nitrobenzene (40 gm.) granulated tin (80 gm.) are placed in a 2-litre, round-bottom flask, fitted with a long air-condenser. 200 c c of concentrated hydrochloric acid are gradually added (about 10 c.c. at a time) through the top of the condenser. The flask is shaken well *after* each addition ; if the liquid begins to boil, the flask must be cooled under the tap to avoid loss of nitrobenzene and aniline. Towards the end, the reaction becomes comparatively slow ; the remaining acid may then be added more quickly. To ensure the complete reduction of nitrobenzene, the flask is heated on a water-bath, until all the oily drops of nitrobenzene and its odour have disappeared.

To liberate the base from the solution containing the stannichloride, $(C_6H_5NH_3)_2[SnCl_6]$, a solution of caustic soda (160 gm. in 230 c.c. of water) is *gradually* added. If during the addition of caustic soda the liquid begins to boil, it must be cooled under the tap. The addition of sodium hydroxide is continued, until the stannic hydroxide, first precipitated, gets completely redissolved, and the mixture shows a strongly alkaline reaction.

The aniline separates out during the above process as a dark oil, and is recovered from the mixture by steam-distillation (p.12, Sec. 8), the distillation being continued until the liquid that passes over is no longer milky, but perfectly clear. The distillate consists of two layers : (*i*) a lower, oily layer of aniline, and (*ii*) an upper, aqueous layer containing aniline in solution and in suspension. The whole of it is saturated with common salt, and then extracted thrice with ether in a separating funnel, using about 50 c.c. for each extraction. The ethereal solution is dehydrated by allowing it to stand over solid KOH[1]. The clear liquid is decanted into a distillation flask, and the ether is distilled off. The residual aniline is now distilled off using an air condenser, and the fraction boiling at 180° to 185° is collected.

Manufacture. Aniline is manufactured by the reduction of nitrobenzene by means of iron and water, in the presence of a little hydrochloric acid—one-fortieth of the theoretical amount required by the equation :

$$C_6H_5NO_2 + 3Fe + 6HCl \rightarrow C_6H_5NH_2 + 3FeCl_2 + 2H_2O.$$

The reaction is explained by assuming that the acid present dissolves

[1]Calcium chloride cannot be used, as it forms solid compounds with amines just as it does with ammonia.

some of the iron to form ferrous chloride. This gets hydrolysed, setting free the acid once again, which, in turn, dissolves more iron, and so on, the iron being ultimately converted into ferrous hydroxide. So, the nascent hydrogen required for the reduction is derived from the action of iron on water, under the catalytic effect of ferrous chloride.

$$Fe + 2HCl \rightarrow FeCl_2 + 2H \quad [\times 3]$$
$$FeCl_2 + 2H.OH \rightleftharpoons Fe(OH)_2 + 2HCl \quad [\times 3]$$
$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O$$
$$C_6H_5NO_2 + 3Fe + 4H_2O \rightarrow C_6H_5NH_2 + 3Fe(OH)_2$$

50 parts of nitrobenzene and 80 parts of water are placed in a cast-iron vessel, *V*, having a bricklining, *B*, and provided with a mechanical stirrer, S and a reflux condenser, C, (Fig. 1). The mixture is heated to boiling by blowing in steam, 2 parts of hydrochloric acid are now added, steam is shut off, and 55 parts of finely ground cast-iron are gradually added for about 8 hours. A vigorous reaction sets in with evolution of large quantities of heat, which keep the mixture boiling actively throughout the time the iron is added.

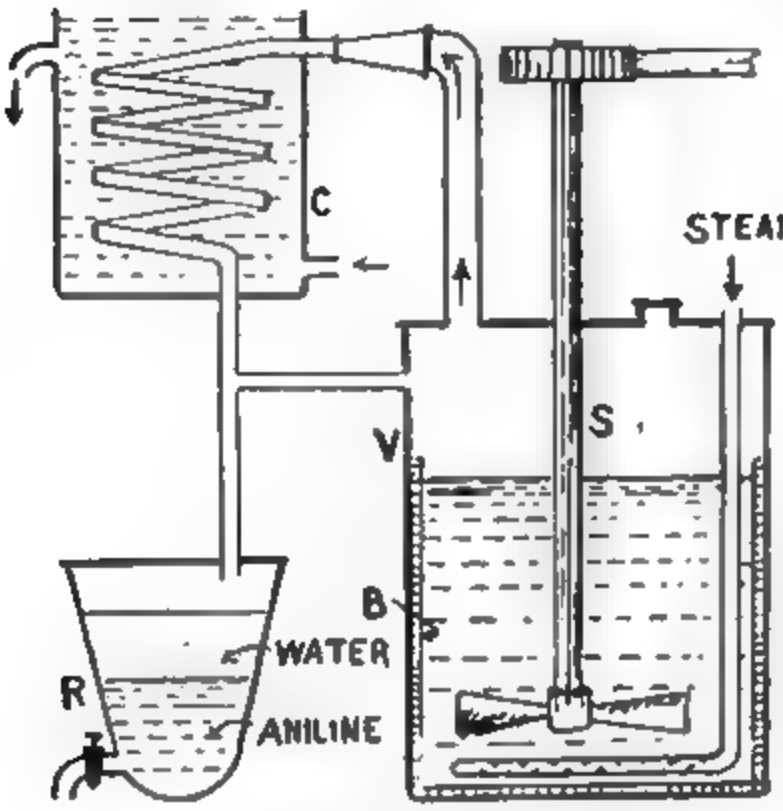


Fig. 1. Diagrammatic Sketch of Plant for the Manufacturer of Aniline.

When all the iron has been added, the heating is continued by steam until the distillate returning from the reflux condenser is no longer yellow (absence of nitrobenzene) but prefectly colourless. Some milk of lime is now added to decompose any aniline hydrochloride produced, and aniline is distilled off in steam and collected in the receiver *R*. Aniline, wich forms the lower layer, is drawn off from time to time. It is then dehydrated by means of solid KOH, and purified by redistillation. The aqueos liquid left in the receiver contains about 3 per cent of dissolved aniline, and is returned to the steam boiler and used for a subsequent aniline distillation.

Physical Properties. When prepared fresh, aniline is a colourless, strongly refractive, oily liquid. It boils at 184°, is slightly soluble in water, and, on exposure to light and air, it gradually turns yellow, becoming ultimately black.

Reactions. The reactions of aniline may be divided into two groups:

(1) **Reactions of the $-NH_2$ Group :—**

(*i*) Aniline is a basic substance, and combines with acids to form salts such as aniline hydrochloride, $C_6H_5.NH_2.HCl$, or $(C_6H_5NH_3)Cl$. However, the electronegative nature of the benzene ring renders aniline even a weaker base than ammonia, being neutral towards litmus (contrast aliphatic amines, which are much stronger bases than ammonia).

(*ii*) *Alkylation.* Like aliphatic amines, aniline reacts with alkyl halides, yielding alkyl derivatives, such as *methylaniline* $C_6H_5.NH(CH_3)$, and *dimethylaniline*, $C_6H_5.N(CH_3)_2$, and also quaternary ammonium compounds, such as a phenyltrimethyl-ammonium iodide, $[C_6H_5N(CH_3)_3]I$.

(*iii*) *Acylation.* Aniline is also acted on by acid chlorides, yielding substituted amides. Thus, with acetyl chloride in forms acetanilide, a substance used in cases of fever for lowering the body temperature.

$$C_6H_5.NH_2 + CH_3COCl \rightarrow \underset{\text{Acetanilide}}{C_6H_5.NH.CO.CH_3} + HCl$$

(*iv*) **Carbylamine Reaction.** When treated with chloroform and alcoholic potash, aniline gives phenyl isocyanide, which possesses a highly obnoxious odour.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$$

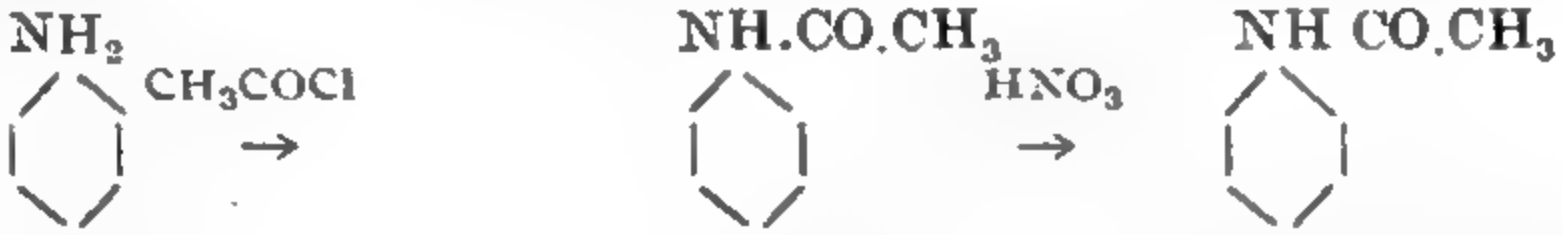
(*v*) **Diazo Reaction.** The most important reaction of aniline, and other aromatic amino compounds containing the—NH_2 group in direct union with the benzene ring, which distinguishes such compounds from aliphatic primary amines, is that when treated with nitrous acid in the *cold*, they form diazonium compounds which are of great practical importance ; *e. g.*,

$$\underset{\text{Aniline}}{C_6H_5NH_2} + HNO_2 + HCl \rightarrow \underset{\substack{\text{Benzene}\\ \text{diazonium chloride}}}{C_6H_5.N_2Cl} + 2H_2O.$$

If the reaction mixture be warmed, the diazonium compound is hydrolysed with the evolution of nitrogen and the production of a phenol:—

$$C_6H_5N_2Cl + H.OH \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + HCl + N_2$$

(2) **Reactions of Benzene Nucleus.** The substitution of the amino-group for hydrogen of the nucleus makes the remaining hydrogen atoms readily replaceable by substituents. Thus, while benzene is only slowly attacked by bromine at the ordinary temperature, aniline is converted by bromine water into *s-tribromoaniline*, $C_6H_2Br_3(NH_2)$. Again, while benzene does not react with iodine except in the presence of oxidizing agents, aniline readily yields *mono-iodoaniline*, $C_6H_4I(NH_2)$. Similarly nitric acid attacks aniline, giving *di*-and *tri-nitranilines*, the reaction proceeding so vigorously that it is not possible to prepare mononitraniline except by previously " protecting " the amino group by acetylation :—



Aniline Acetanilide *p*-Nitro-acetanilide

The product, on being hydrolysed, yields *p-nitraniline*, $C_6H_4 \begin{matrix} /NH_2\ (1) \\ \backslash NO_2\ (4) \end{matrix}$

In the same manner we can prepare *p*-chloro-and *p*-bromo-anilines.

Expt. 2. *Tests of Aniline:*—

1. *Carbylamine Reaction.* Take a drop each of aniline and chloroform in a test tube. Add a few drops of alcoholic potash, and warm the mixture. A disgusting odour of phenyl isocyanide is evolved.

2. *Diazo Reaction.* If to some well-cooled solution of aniline in dilute hydrochloric acid we add gradually a solution of sodium nitrite, we get a solution of phenyl-diozonium chloride. On warming a portion of this solution, nitrogen will be evolved and the liquid will develop the characteristic odour of carbolic acid. If to a second portion of the diazotized solution a few drops of an alkaline solution of β-naphthol be added, a scarlet red precipitate will be formed.

3. *Bromination.* If bromine water be added to an aqueous solution of aniline we get pinkish precipitate of tribromo-aniline, which turns grey green.

4. *Hypochlorite Test.* If a solution of sodium hypochlorite (or of bleaching powder) be added to an aqueous solution of aniline, a transient purple-violet coloration is developed.

5. *Formation of Aniline-black.* If a few drops of potassium dichromate solution

be added to a solution of aniline in dilute sulphuric acid, a deep-blue or black colour is produced, owing to the formation of "aniline-black".

Uses. Aniline is one of the compounds having greatest practical importance, It is used in the manufacture of dyes and a very large number of benzene derivatives.

4. Comparison between Aniline and Methylamine. These two compounds resemble one another in the following points :—

1. Both are basic in nature, and form salts with acids.
2. When treated with alkyl halides, they give alkyl derivatives.
3. With acid chlorides, they yield substituted amides.
4. They both give carbylamine reaction.

Aniline differs from methylamine in the following points :—

1. It cannot be prepared by the action of ammonia on chlorobenzene.
2. It is comparatively insoluble in water.
3. It is a much weaker base, and has no effect on litmus. Nor does it precipitate the hydroxide of heavy metals from solutions of their salts.
4. It reacts with nitrous acid in the *cold*, yielding a diazonium salt. Methylamine gives methyl alcohol and nitrogen.
5. It reacts with bromine, nitric acid, etc., giving products in which the hydrogen of the benzene nucleus is replaced (see *p.* 259).
6. It gives a purple-violet colour with aqueous sodium hypochlorite. Methylamine does not give this reaction.
7. When treated with aqueous potassium dichromate and dilute sulphuric acid it gives a deep-blue or black colour. Methylamine does not give this test.

Aniline Hydrochloride, or *Anilinium Chloride*, $(C_6H_5NH_3)Cl$. This is a colourless, crystalline salt, so soluble in water that it is not easily precipitated by excess acid. It is readily isolated by passing dry HCl gas into a solution of aniline in ether, the separation being quantitative owing to the insolubility of the salt in this solvent. The salt has a sharp melting point (198°), and is distillable (b.p., 245°).

Aniline hydrochloride is employed in calico printing. The cloth is printed with a mixed solution containing aniline hydrochloride, potassium chlorate, cupric sulphate and gum arabic. On exposure to air, oxidation of aniline to *aniline black* occurs, and a black print is the result.

5. Acetanilide, *Phenyl-acetamide*, $C_6H_5.NH.CO.CH_3$. This important derivative of aniline is prepared by heating aniline with glacial acetic acid :—

$$C_6H_5.NH\,H + HO.CO.CH_3 \rightarrow C_6H_5.NH.CO.CH_3 + H_2O.$$

A mixture of equal weights of pure aniline and glacial acetic acid, together with about 3% of anhydrous zinc chloride is gently boiled for about an hour in a flask fitted with a reflux condenser. The reaction mixture, while still hot, is poured into a large quantity of cold water, and the precipitated acetanilide is filtered, and washed with cold water. It is then dissolved in boiling water, a little animal charcoal is added to the solution, which is then filtered at the boiling point. On allowing the filtrate to cool, the acetanilide comes out in shining colourless plates.

Acetanilide crystallizes in glistening plates (m. p. 112°). It is sparingly soluble in cold water and readily so in hot water.

Dilute acids and alkalies hydrolyse acetanilide, producing aniline and acetic acid. Acetanilide is employed in medicine, under the name of **antifebrin**, for lowering the body temperature during fever.

6. *m*-Nitraniline, This compound is prepared by the *partial* reduction of *m*-dinitrobenzene by means of ammonium sulphide. It is an orange coloured, crystalline solid, melting at 114°. It is sparingly soluble in water, but readily dissolves in alcohol. When reduced with tin and hydrochloric acid, *m*-nitraniline gives ***m*-phenylene diamine,** $C_6H_5 < \begin{matrix} NH_2\ (1) \\ NH_2\ (3) \end{matrix}$

7. Benzylamine, $C_6H_5CH_2NH_2$. Benzylamine is an example of a compound containing the amino-group in the *side-chain* and closely resembles aliphatic amines in its modes of preparation and properties. Thus it may be obtained :—

(*i*) by the action of ammonia on benzyl chloride,

$$C_6H_5CH_2Cl + NH_3 \rightarrow C_6H_5.CH_2.NH_2 + HCl,$$

(*ii*) by the reduction of phenyl cyanide,

$$C_6H_5CN + 4H \rightarrow C_6H_5CH_2.NH_2.$$

(*iii*) from phenylacetamide, by the bromamide reaction,

$$C_6H_5CH_2CO.NH_2 \xrightarrow{Br_2 + KOH} C_6H_5.CH_2.NH_2.$$

Properties. Benzylamine is a colourless, pleasant smelling liquid. It readily dissolves in water yielding a strongly alkaline solution.

It forms salts with acids, gives carbylamine reaction, and when treated with nitrous acid, it gives benzyl alcohol and *not* a diazo compound.

8. Methylaniline, $C_6H_5.NH.CH_3$. This is an example of a mixed aliphatic-aromatic *secondary* amine.

Preparation. Methylaniline is obtained from *pure* aniline in the following steps :—

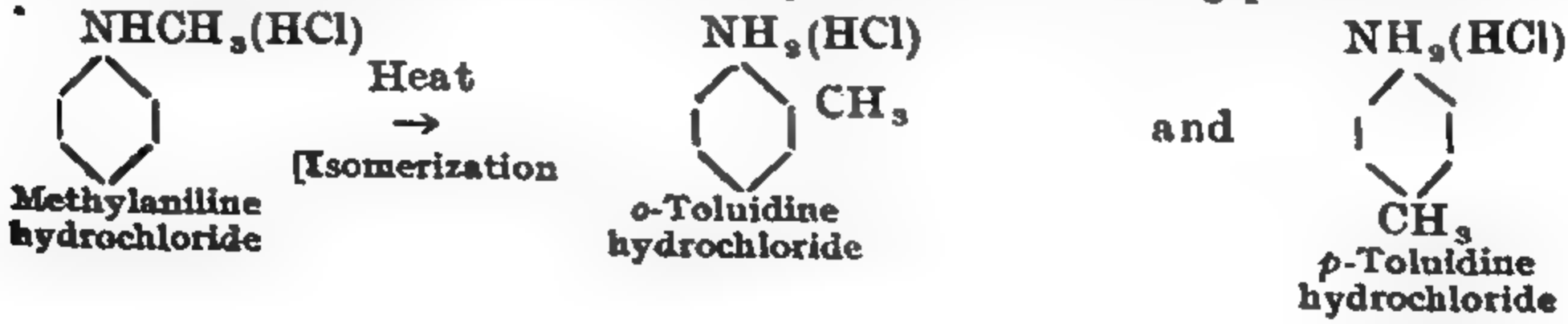
$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{\text{Glacial acetic acid}} \underset{\text{Acetanilide}}{C_6H_5.NH.COCH_3} \xrightarrow{Na} \underset{\text{Sodio-acetanilide}}{C_6H_5.NNa.COCH_3}$$

$$\xrightarrow{CH_3I} \underset{\text{Methyl acetanilide}}{C_6H_5.N(CH_3).COCH_3} \xrightarrow{KOH(Aq)} \underset{\text{Methylaniline}}{C_6H_5.NH.CH_3}$$

Properties. (1) Methylaniline is a colourless liquid (b. p. 193°). It is a stronger base than aniline, and readily combines with acids, forming salts.

(2) Being a secondary amine, it reacts with nitrous acid yielding *methyl-phenyl-nitrosamine*, $C_6H_5.N(NO).CH_3$, a yellow oily liquid, which gives Liebermann's nitroso-reaction (*p.* 171).

(3) When methylaniline hydrochloride is heated to 300° in an autoclave, the alkyl group migrates from the side-chain to the nucleus, a mixture of the hydrochlorides of ortho- and paratoluidines being produced :—



Methylaniline hydrochloride — o-Toluidine hydrochloride — p-Toluidine hydrochloride

9. Dimethylaniline, $C_6H_5.N(CH_3)_2$.

Preparation. This compound is prepared on a large scale by heating aniline hydrochloride with an excess of methyl alcohol in an autoclave (methylation) :—

$$\underset{\text{Aniline hydrochloride}}{C_6H_5NH_2HCl} + 2CH_3OH \rightarrow \underset{\text{Dimethylaniline hydrochloride}}{C_6H_5.N(CH_3)_2HCl} + 2H_2O$$

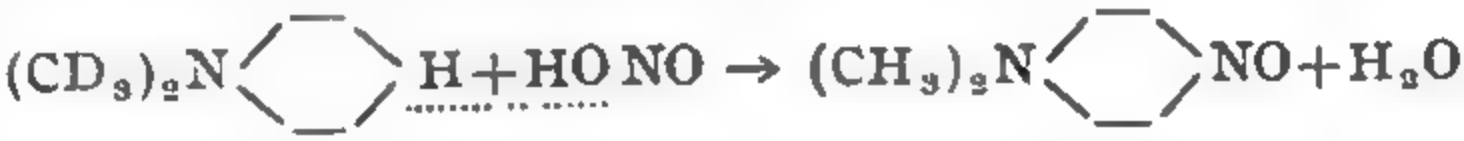
The product is treated with milk of lime to set free the base, which is then separated by distillation in steam.

Properties. (1) Dimethylaniline is an oily liquid of a peculiar odour. It boils at nearly the same temperature (192°) as methylaniline.

(2) It is even a stronger base than methylaniline.

(3) Like other tertiary amines, dimethylaniline combines with alkyl halides yielding *quaternary ammonium salts*.

(4) Dimethylaniline differs from aliphatic tertiary amines and from *purely* aromatic tertiary amines, *e.g* , triphenylamine, $(C_6H_5)_3N$, in being able to react with nitrous acid, yielding intensely green *p*-nitrosodimethylaniline. In this reaction the para hydrogen atom of dimethylaniline is replaced by the nitroso-group, NO :—



Dimethylaniline — Nitrous acid — *p*-Nitroso-dimethylaniline

Use. Dimethylaniline is extensively employed in the manufacture of dyes.

10. Distinction between Primary, Secondary, and Tertiary Amines. In this chapter we have studied four different aromatic amines; namely—

(1) *Aniline*, NH_2, which is a primary amine having the $—NH_2$ group directly linked to the benzene nucleus.

(2) *Benzylaniline*, CH_2NH_2, which is also a primary amine, but has the $—NH_2$ group in the side-chain.

(3) *Methylaniline*, $NH.CH_3$, which is a mixed alphyl-aryl secondary amine.

(4) *Dimethylaniline*, $N(CH_3)_2$, which is a mixed alphyl-aryl tertiary amine.

The distinctive reactions of the above four classes of amines and those of the purely aliphatic primary, secondary and tertiary amines (compare Sec. 6, p. 171) are summarized in the table on page 263.

Distinction between Primary, Secondary and Tertiary Amines :—

Reaction	Primary Amines			Secondary Amines		Tertiary Amines	
	$C_6H_5NH_2$	$C_6H_5.CH_2NH_2$	$CH_3.NH_2$	$C_6H_5.NH.CH_3$	$(CH_3)_2NH$	$C_6H_5N(CH_3)_2$	$(CH_3)_3N$
(1) Nitrous acid.	Gives a diazonium salt in the *cold*.	Gives benzyl alcohol and nitrogen,	Gives methyl alcohol and nitrogen.	Gives nitrosamine (yellow oil),	Also gives a nitrosamine,	Gives *p*-nitroso dimethyl aniline (bright green ecrystals),	No action
(2) Methyl-iodide.	Reacts with 3 molecules of CH_3I to give phenyltrimethyl ammonium iodide.	Also reacts with 3 molecules of CH_3I.	Reacts with 2 molecules of CH_3I yielding tetramethyl ammonium iodide.	Reacts with 2 molecule of CH_3I, giving phenyltrimethyl ammonium iodide.	Reacts with 2 molecules of CH_3I giving tetramethyl ammonium iodide.	Takes up one molecule of CH_3I.	Also takes up one molecule of CH_3I
(3) Benzene sulphonic chloride.	Gives $C_6H_5SO_2.NHC_6H_5$ soluble in KOH).	Gives $C_6H_5SO_2NH(CH_2C_6H_5)$ soluble in KOH).	Gives $C_6H_5SO_2.NH(CH_3)$ (soluble in KOH)	Gives $C_6H_5SO_2.N(CH_3)C_6H_5$ (insoluble in KOH).	Gives $C_6H_5SO_2.N(CH_3)_2$ (insoluble in KOH).	No action.	No action
(4) Carbylamine reaction.	All three give the carbylamine reaction.			Do not give carbylamine reaction.			

QUESTIONS

1. Give a description with full practical details of a method of preparing aniline from benzene, and describe how you would prepare from it any derivative you may choose ? *(Punjab, Inter., 1914)*

2. Describe the commercial preparation and purification of aniline. Give its tests and uses. *(Punjab, Inter., 1940)*

3. Describe the separate action of chlorine, nitric acid, sulphuric acid, and nitrous acid upon aniline. *(Punjab, B. Sc., 1924)*

4. How would yon prepare a specimen of acetanilide in the laboratory ? *(Punjab, B. Sc., 1922)*

5. A colourless crystalline solid was found to contain C=71·1%, H 6·7% N=10.4%. On boiling the substance with concentrated hydrochloric acid and adding an excess of KOH, an oily liquid was obtained, which gave a violet coloration with a solution of sodium hypochlorite. What was the original substance ? [*Ans.* Acetanilide, $C_6H_5.NHCOCH_3$.]

6. How will you convert aniline into (*a*) *p*-toluidine (*b*) *p*–nitraniline, and (*c*) *p*-nitroso-dimethylaniline ?

7. What products can be obtained by the action of the methyl iodide on aniline ? State the action of nitrous acid on each, and show by formulae the changes which occur when their hydrochlorides are heated under pressure. *(Panjab, B. Sc., 1933)*

8. How is methylaniline prepared from aniline ? Give its chief chemical properties. How would you distinguish between aniline and methylaniline ?

9. How is methylaniline prepared on a commercial scale ? To what use is it put ? Describe the reaction which differentiate dimethylaniline from (*a*) triphenylamine and (*b*) trimethylamine.

10. Give in a tabular form the chief reactions in which primary, secondary and tertiary amines (aliphatic and aromatic) differ from and resemble each other.

CHAPTER 31

DIAZONIUM SALTS

1. Diazo-reaction. The most characteristic property of an aromatic amino-compound, containing the amino group in *direct* union with the carbon of the nucleus, is that when a *well-cooled* aqueous solution of one of its salts is treated with nitrous acid, a "*diazonium salt*" is produced.

$$\underset{\text{Aniline hydrochloride (or anilinium chloride)}}{[C_6H_5.NH_3]\,Cl} + HNO_2 \rightarrow \underset{\text{Benzene diazonium chloride}}{[C_6H_5.{\equiv}N]Cl} + 2H_2O$$

The above reaction, called **diazo-reaction,** or "**diazotization**" of an amino compound, was discovered by Griess[1] in 1858, and is perhaps the most important reaction in the chemistry of aromatic compounds. The diazonium salts are of great importance in organic synthesis and in the manufacture of dyes, as they undergo a number of remarkable reactions.

2. Preparation. (1) The diazonium salts may be obtained in *crystalline* state by treating a well-cooled solution of an amino compound in absolute alcohol with amyl-nitrite[2] and a mineral acid, the reaction being carried out, so far as possible, in the *absence* of water. Thus, to prepare **benzene diazonium sulphate** the following procedure is adopted :

Aniline (1½ part) is dissolved in absolute alcohol (1 part), and concentrated sulphuric acid (2 parts) is added to the solution. The mixture is cooled in freezing mixture and pure amyl nitrite (2 parts) is gradually run in from a tap funnel. On allowing the reaction mixture to stand for about 15 minutes, crystals of benzene diazonium sulphate separate out. They may be washed with alcohol and ether and dried in air at the ordinary temperature.

Crystals of the *chloride* may be obtained in a similar manner, hydrogen chloride being used instead of sulphuric acid. The *nitrate*[3] is best obtained by passing nitrogen trioxide (generated by heating nitric acid with arsenious oxide) into a solution of aniline in dilute nitric acid. On adding alcohol and ether, crystals of the nitrate separate out.

(2) *Preparation of a Solution of a Diazonium Salt.* Since the diazonium salt in the dry state are very explosive, and since most of reactions that they undergo readily take place in aqueous solution, they are almost invariably prepared in aqueous solution. The amino compound is dissolved in an excess of a mixture of equal volumes of concentrated hydrochloric acid and water, and the mixture is well-cooled by means of ice. A well-cooled aqueous solution of sodium nitrite is gradually run in from a dropping funnel, the end of which dips under the solution to be diazotized[4]. Throughout the addition the mixture is well stirred, and the temperature not allowed to rise. The addition of sodium nitrite is continued, until a drop of the

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[1] Johann Peter Griess (1829-1888) was a German chemist employed in an English brewery. He carried out his researches in his spare time, and is well known for his work on the diazo compounds.

[2] Amyl nitrite is here used instead of sodium nitrite because of its solubility in alcohol.

[3] The salt is violently explosive, and it is *not* advisable to prepare more than half a gram in the dry state.

[4] The process of the conversion of an amino-compound into a diazonium salt is known as *diazotization*.

reaction mixture gives an *immediate* blue colour when placed upon starch-potassium-iodide paper showing the presence of free nitrous acid.

3. Physical Properties. Diazonium salts are colourless crystalline substances, very readily soluble in water, less soluble in alcohol. When in the dry state, they explode violently on being heated or struck. They are true salts in all respects, and the conductivities of their aqueous solutions are comparable to those of the ammonium salts.[1]

4. Reactions. The reactions of the diazonium salts may be divided into two groups :—

(*A*) **Replacement of the diazo group,—N_2X, by simple groups or atoms.** By treating the solutions of diazonium salts with different reagents the diazo group is readily replaced by other substituents, *nitrogen being set free in gaseous state.* The following of these substitution reactions are the more important :—

(1) *Replacement by Hydrogen.* When the solution of a diazonium salt is warmed with an alkaline solution of stannous chloride, the diazo group gets replaced by a hydrogen atom, and an aromatic hydrocarbon is produced :—

$$\underset{\text{Benzene diazonium chloride}}{C_6H_5.N_2Cl} + 2H \rightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + HCl$$

When a dry diazonium salt is heated with alcohol, there occurs, in addition to the formation of an ether (reaction 2), a replacement of the—N_2X group by hydrogen with production of an aromatic hydrocarbon, the alcohol being oxidized to acetaldehyde.

$$C_6H_5N_2Cl + CH_3.CH_2OH \rightarrow C_6H_6 + N_2 + HCl + CH_3CHO$$

(2) *Replacement by Hydroxyl, Alkoxyl or Acyloxyl Group.* When the aqueous solution of a diazonium salt is warmed, hydrolysis of the compound occurs with the production of a phenol :—

$$C_6H_5N_2Cl + H.OH \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

When a dry diazonium salt is heated with an alcohol or a fatty acid, an ether or an ester is produced.

$$C_6H_5N_2Cl + H.OC_2H_5 \rightarrow \underset{\text{Phenatole}}{C_6H_5.O.C_2H_5} + N_2 + HCl$$

$$C_6H_5N_2Cl + HO.CO.CH_3 \rightarrow \underset{\text{Phenyl acetate}}{C_6H_5O.CO.CH_3} + N_2 + HCl$$

(3) *Replacement by Iodine.* When a solution of a diazonium salt is warmed with potassium iodide, the corresponding iodo-derivative is produced :—

$$C_6H_5N_2Cl + KI \rightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + N_2 + KCl$$

The reaction is often employed as a preparative method for the aromatic iodo-compounds.

(4) *Replacement by Chlorine, Bromine or the Cyanogen Group.* When a solution of diazonium salt is warmed with a solution of cuprous chloride in hydrochloric acid, the diazo-group is replaced by a chlorine atom, and a chloro-derivative of an aromatic hydrocarbon results :—

[1] They further resemble ammonium compounds in the formation of complex salts, such as the platinichlorides, $(Ar.N_2)_2PtCl_6$.

$$C_6H_5N_2Cl(+CuCl) \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2$$

Similarly, when we use a solution of cuprous bromide in hydrobromic acid or a solution of potassium cuprous cyanide, we get the cyano derivative :—

$$C_6H_5N_2Cl + CuBr \rightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2 + CuCl$$

$$C_6H_5N_2Cl + CuCN \rightarrow \underset{\substack{\text{Phenyl cyanide}\\ \text{(Benzonitrile)}}}{C_6H_5CN} + N_2 + CuCl$$

A reaction like the above, in which a cuprous salt plays the part of a catalyser, is known as **Sandmeyer's reaction**. A modification of it, known as **Gattermann's reaction**, as based on the use of finely-divided copper in place of the cuprous salt.

The conversion of diazonium salts into cyano-compounds is of importance, since these compounds on hydrolysis yield the aromatic acids.

(*B*) **Reactions without elimination of nitrogen.** In addition to the replacement reactions described above, diazonium salts undergo certain other valuable reactions :

(1) *Addition of Bromide.* Diazonium bromides directly add on a molecule of bromine, yielding perbromides.

$$C_6H_5N_2Br + Br_2 \rightarrow C_6H_5.N_2Br_3.$$

(2) *Addition of Hydrogen.* When reduced with a solution of stannous chloride in hydrochloric acid, they yield monosubstituted hydrazines; *e.g.*,

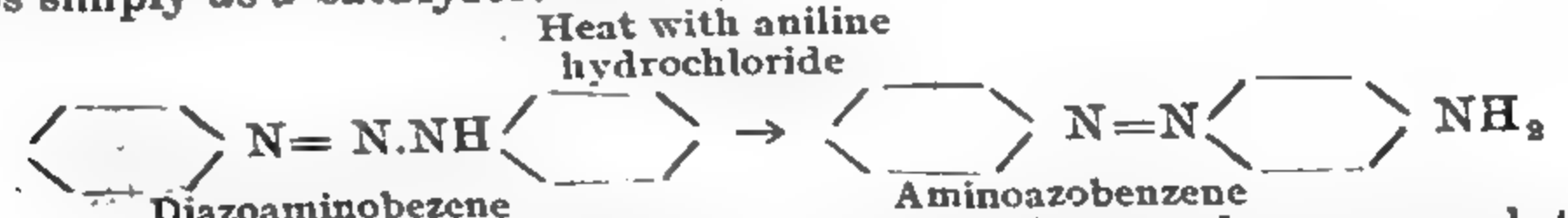
$$\underset{\substack{\text{Benzene diazo-}\\ \text{nium chloride}}}{C_6H_5.N_2.Cl} + 4H \rightarrow \underset{\substack{\text{Phenyl-hydrazine}\\ \text{hydrochloride}}}{C_6H_5.NH.NH_2.HCl}$$

(3) *Condensation with Amines and Phenols.* These reactions are of the highest importance and are employed in the manufacture of **azo-dyes.** The reaction of a diazotized solution of an amino-compound with phenols and amines is called **coupling.** The following are the typical coupling reactions :

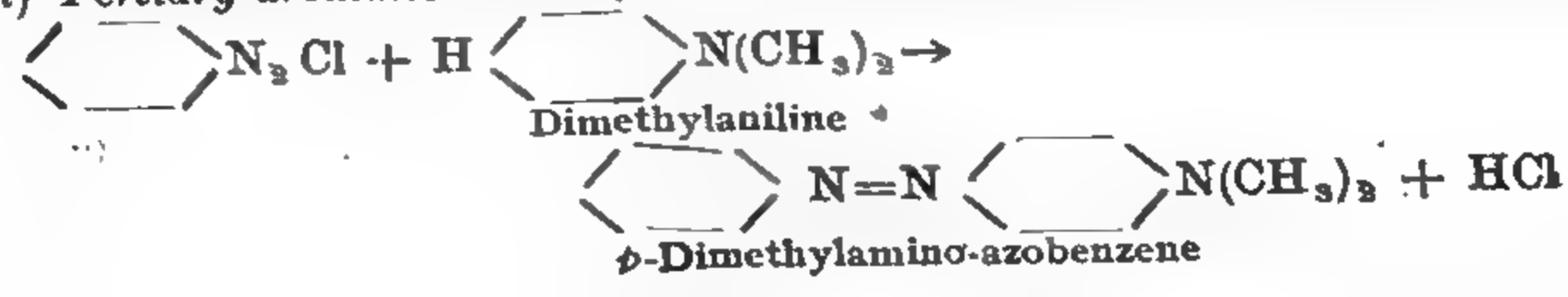
(*i*) *Primary and secondary amines* react with diazonium salts, yielding **diazoamino-compounds** :—

$$\underset{\substack{\text{Benzene}\\ \text{diazonium chloride}}}{C_6H_5N_2Cl} + \underset{\text{Aniline}}{H_2N.C_6H_5} \rightarrow \underset{\text{Diazoaminobenzene}}{C_6H_5.N_2NH.C_6H_5} + HCl$$

The most striking property of the diazoamino-compounds is their isomerization into **aminoazo compounds,** the diazo-group migrating to the *para* position in the ring. The change is usually effected by heating the diazoamino-compound with a little aniline hydrochloride which acts simply as a catalyser. Thus,

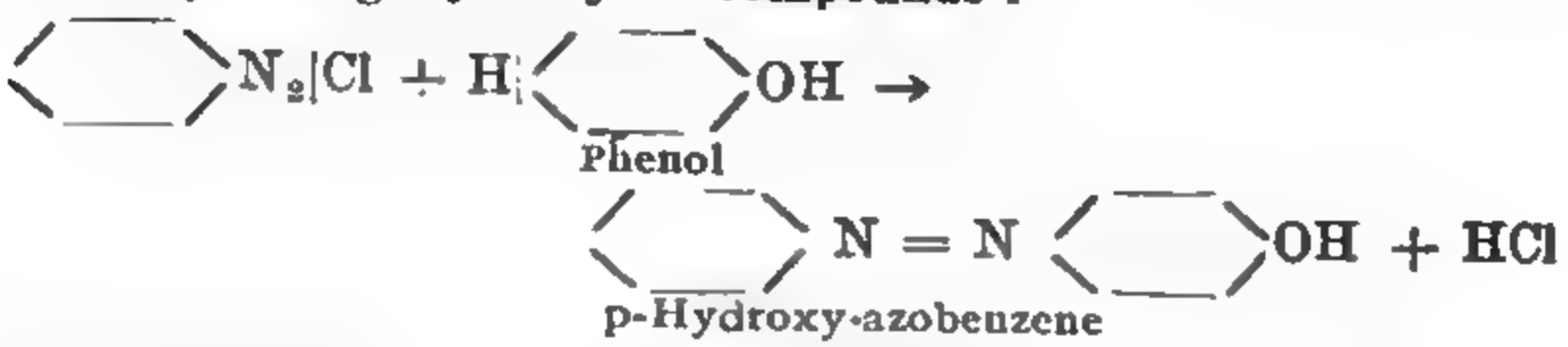


(*ii*) *Tertiary aromatic amines,* in the form of neutral aqueous solutions



of their salts, react with diazonium salts yielding **aminoazo compounds :**

(*iii*) *Phenols*, dissolved in alkalies, undergo coupling with diazonium salts, yielding **hydroxyazo compounds :**



5. **Constitution.** (1) That only *one* of the two nitrogen atoms is directly linked to the nucleus is shown by the conversion of diazonium salts into *mono*-hydric phenols, *mono*-halogen derivatives, etc and their reduction to *mono*-substituted hydrazines, such as $C_6H_5.NH.NH_2$.

SIR WILLIAM HENRY PERKIN (1838-1907)
The "Father of the Dyestuffs Industry"

(2) From their close resemblance with the ammonium compounds in the conductivities of their solution (*p* 265) and the formation of platinichlorides, etc. (*see* foot-noto 1. *p.* 265) Blomstrand assigned an analogous structure to these compounds.

According to modern theory, the ammonium ion is given the structure:—

$$\left[\begin{array}{c} H \\ H{:}\ddot{N}{:}H \\ \ddot{H} \end{array}\right]^+$$

in which the nitrogen atom is tetra-covalent. Hence, the diazonium ion must be assigned the structure :

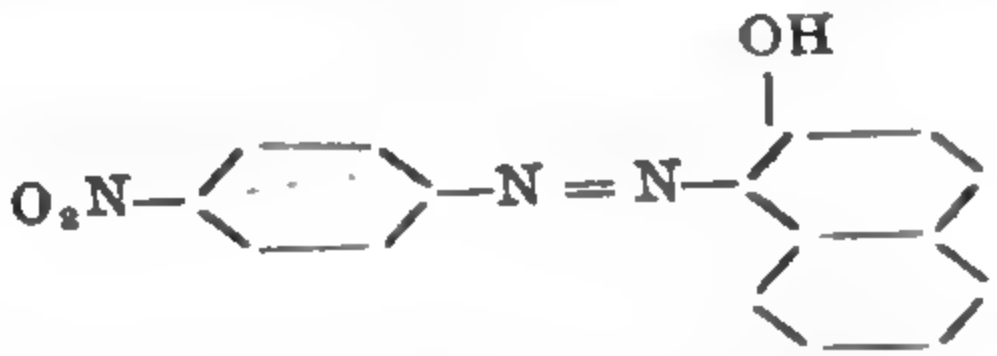
$$[Ar - N \equiv N]^+$$

It is evident that one of the nitrogen atoms in the diazonium ion is tricovalent and the other tetracovalent.

6. Uses Diazonium salts are of great importance in synthetic organic chemistry and are us-d in the preparation of numerous derivatives of aromatic hydrocarbons (refer to reactions). Since the diazonium salts are obtained from the nitro-compounds *via*, the amino-compounds, it is evident that nitration of aromatic substances is a reaction of first rate importance, as, with the help of the diazo-reaction, the nitro-group may b· replaced by almost any desired group. The great importance of diazonium salts in industry is shown by an almost unlimited number of azo-dyes placed on the market.

7. Use of Azo-Dyes in Dyeing and Calico Printing. The fastness to washing of cloth dyed with an azo-colour is the greater the higher the degree of insolubility of the azo-dye Hence, azo-dyes insoluble in water are directly produced on the fabric. Cloth is soaked in an alkaline solution of a phenol (usually beta-naphthol), wrung out, dried, and then immersed in an ice-cold solution of the diazonium salt. Coupling takes place with the production of an azo-dye within the pores of the fabric. Since the diazonium salt solutions must be kept in ice, the colours thus produced are called **ice colours**

A typical example of a dye of this class is ***p*-nitraniline red** (or Para Red) .



which has a brilliant red colour comparable to alarazin. Some other ice colours in common use are :—

β-naphthol + m-Nitroaniline → Nitroaniline Orange
β-naphthol + 2, 4-Dinitroaniline → Permanent Red 2G
β-naphthol + *α*-naphthylamine → Ice Bordeaux (claret)

In calico printing, a paste is made of an alkaline solution of beta-naphthol and a "thickening" material, such as starch, British gum, albumen, casein or glue. The desired design is made on the cloth with this paste, using a **hand block** or an **engraved cylinder.** The fabric after being dried is then passed through an ice-cold bath of a diazonium salt, when the desired pattern or design, consisting of one or more ice colours, is developed on the cloth.

8. Phenylhydrazine. $C_6H_5.NH.NH_2$. This compound is prepared by the reduction of benzene-diazonium chloride by means of stannous chloride dissolved in hydrochloric acid,

$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + 4H \rightarrow \underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5NH.NH_2.HCl},$$

followed by treatment of the hydrochloride with caustic potash to liberate the free base :—

$$[C_6H_5.NH.NH_2]\,HCl + KOH \rightarrow C_6H_5.NH.NH_2 + KCl + H_2O$$

Phenylhydrazine is a colourless oily liquid which turns brown in air

and boils with slight decomposition at 241°. On cooling it solidifies to form colourless crystals (m.p. 23°). It is only slightly soluble in water.

Reactions. (1) Phenylhydrazine is a strong base and combines with acids to form salts, *e.g.*,

$$\underset{\text{Phenylhydrazine}}{C_6H_5.NH.NH_2} + HCl \rightarrow \underset{\text{Phenylhydrazinium chloride}}{[C_6H_5NH.NH_3]Cl}$$

(2) It is an active reducing agent and precipitates cuprous oxide from Fehling's solution.

(3) Phenylhydrazine is an important reagent for aldehydes, ketones, and sugars. Its reactions with these substances have already been described in their proper places.

QUESTIONS

1. Write notes on : (*a*) Sandmeyer's reaction, (*b*) Diazotization, (*c*) Coupling, and (*d*) Gattermann's reaction.

2. Describe the preparation of the *diazo-compounds*, and give their chief reactions. What are the industrial uses of diazo-compounds ?
(*Punjab, Inter., 1933; 1930*)

3. How will you effect the following conversions :— (*i*) Nitrobenzene into benzoic acid, (ii) aniline into iodobenzene, (*iii*) benzene into phenylhydrazine, and (*iv*) aniline into *p*–dimethylamine-azobenzene ?

4. Explain the uses of diazo-compounds in synthesizing organic compounds. Illustrate your answer by quoting, with examples, *six* different and characteristic reactions of this class of compounds. (*Punjab, Inter., 1926*)

5. What is diazotization ? Starting from aniline, how would you prepare benzene diazonium chloride solution ? How would you use this solution to prepare (*a*) benzene (*b*) chlorobenzene, (*c*) iodobenzene (*d*) benzoic acid, and (*e*) phenylhydrazine ? (*Punjab, Inter., 1943*)

CHAPTER 32

AROMATIC SULPHONIC ACIDS

1. Formation. When benzene or one of its derivatives is heated with concentrated sulphuric acid (or fuming sulphuric acid containing varying proportions of SO_3) the hydrogen of the nucleus is replaced by the sulphonic group, $—SO_2.OH$. The product is called a *sulphonic acid* and the process sulphonation.

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 \rightarrow \underset{\text{Benzene Sulphonic acid}}{C_6H_5.SO_2OH} + H_2O$$

$$\underset{\text{Aniline}}{C_6H_5.NH_2} + H_2SO_4 \rightarrow \underset{\text{Aniline-}p\text{-sulphonic acid}}{C_6H_4<^{NH_2}_{SO_2OH}} + H_2O$$

$$C_6H_6 + 2H_2SO_4 \rightarrow \underset{\text{Benzene-}m\text{-disulphonic acid}}{C_6H_4<^{SO_2OH}_{SO_2OH}} + 2H_2O.$$

The number of sulphonic groups introduced into the molecule depends (as in the case of nitro-groups) on the temperature, the concentration of the acid, and on the nature of the substance undergoing sulphonation. In the case of benzene, at the most three sulphonic groups may thus be introduced into the molecule.

From the strongly acidic reaction mixture sulphonic acids may separate out as crystals on cooling. If this does not occur, they may be separated from the mixture containing excess of sulphuric acid by the addition of common salt, until no more of it dissolves. Under these conditions the sulphonic acid is precipitated as its sodium salt. This is separated, dissolved in water, the solution treated with an equivalent quantity of a mineral acid and the free sulphonic acid extracted with ether. Another method of separating sulphonic acids is based on the solubility of their barium salts in water, (*see* under Benzene-sulphonic acid, Sec. 4).

Sulphonation may also be effected by means of chlorosulphonic acid, sulphuryl chloride or with a mixture of sulphuric acid with another dehydrating agent, such as acetic anhydride.

2. Manufacture. The process of sulphonation is of great technical importance, especially in the manufacture of dyes. This is based on the ready solubility of sulphonic acids, and more particularly of their sodium salts in water. Many compounds of beautiful colour, that cannot be used as dyes because of their insolublility in water, are rendered available for dyeing purposes after sulphonation.

The technical preparation of sulphonic acids is carried out in large enamelled, or lead-lined pans (Fig. 1). This is usually provided with an outer jacket through which steam or cold water can be circulated to control the temperature. If the compound to be sulpho-

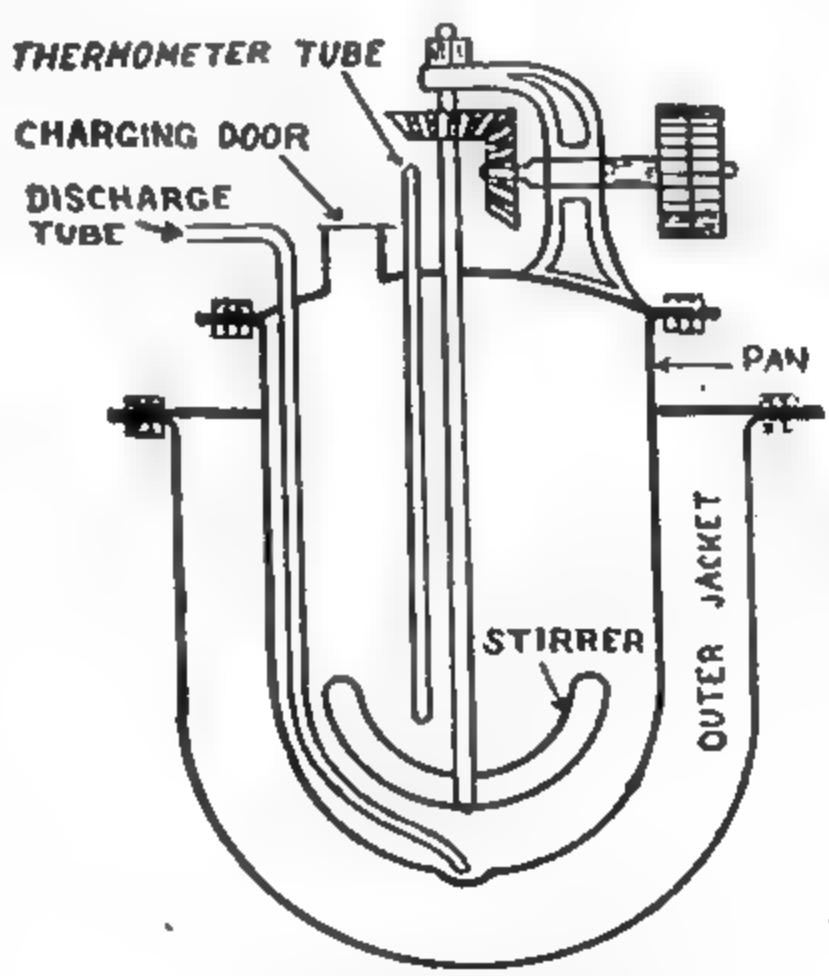


Fig. 1. Sulphonation Pan.

nated is volatile, the pan is also fitted with a reflux condenser (compare technical preparation of Aniline, Fig. 1, page 258). At the end of the opera ion, the charge is blown by compressed air into water contained in large vats, and the sulphonic acid is recovered either as such or as the sodium salt.

3. Properties and Chemical Behaviour. (1) Sulphonic acids are colourless, crystalline substances, very readily soluble in water, and are usually hygroscopic.

(2) They are strong acids, and their salts (including the barium salts) are soluble in water.

(3) When a sulphonic acid is treated with phosphorus pentachloride, hydroxyl part of the sulphonic group is replaced by chlorine, with the production of a **sulphonic chloride** :

$$\underset{\text{Benzene-sulphonic acid}}{C_6H_5.SO_2OH} + PCl_5 \rightarrow \underset{\text{Benzene-sulphonic chloride}}{C_6H_5.SO_2Cl} + POCl_3 + HCl.$$

(4) When fused with an alkali hydroxide, they give *phenols*, the sulphonic group being replaced by the hydroxyl group :

$$C_6H_5\ SO_2OK + KOH \rightarrow C_6H_5.OH + K_2SO_3.$$

The reaction is of great technical importance.

(5) When their potassium salts are distilled with potassium cyanide, the corresponding nitriles are produced :—

$$C_6H_5.SO_2OK + KCN \rightarrow C_6H_5\ CN + K_2SO_3.$$

The reaction may be utilized for synthesizing aromatic acids :

$$C_6H_5CN + 2H_2O \rightarrow C_6H_5COOH + NH_3$$

(6) Lastly, the sulphonic group may be replaced by *hydrogen*. This is effected by passing superheated steam into the acid, or by heating it at 150° with concentrated hydrochloric acid in a sealed tube:

$$\begin{matrix} C_6H_5.SO_2.OH \\ +H\,OH \end{matrix} \rightarrow C_6H_6 + H_2SO_4.$$

4. Benzene-sulphonic Acid, $C_6H_5SO_2OH$. Benzene-sulphonic acid is prepared in the laboratory by the interaction of benzene and fuming sulphuric acid :—

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5.SO_2OH + H_2O$$

Benzene (1 part) is added gradually, with continued shaking, to fuming sulphuric acid (4 parts) contained in a flask, the latter being fitted with a reflux condenser. Care must be taken that each quantity of benzene gets dissolved before any further amount is added.

When all the benzene has dissolved, the reaction mixture is poured into an excess of water, and then neutralized with barium carbonate made into a thin paste with water. The liquid is heated, and quickly filtered through a fluted filter, and then allowed to cool. Barium benzene sulphonate that crystallizes out is purified by recrystallization from hot water.

To obtain free benzene sulphonic acid a weighed amount of the crystals is treated with the calculated quantity of dilute sulphuric acid. The precipitated barium sulphate is filtered off, the solution evaporated to a small bulk, and the benzene sulphonic acid is allowed to crystallize preferably in a desiccator.

In the preparation of benzene sulphonic acid on a large scale, concentrated sulphuric acid is used instead of the fuming acid, but the reaction is much slower and the mixture requires heating and stirring.

Properties. Benzene sulphonic acid crystallizes from water with $1\frac{1}{2}$ H_2O in colourless, hygroscopic plates (m p. 66°). It possesses all the chemical characters of aromatic sulphonic acid.

Use. Benzene-sulphonic acid is employed in the manufacture of metanilic acid (*m*-aminobenzene-sulphonic acid).

5. Benzene Sulphonic Chloride, $C_6H_5SO_2Cl$. This is the acid chloride of benzene sulphonic acid from which it is obtained by the action of phosphorus pentachloride (Reaction 3, Chap. 4 Sec. 6).

Benzene sulphonic chloride is a liquid with a disagreeable odour. It boils at 251°. Like other acid chlorides it reacts with water, alcohol, ammonia, and primary and secondary amines :—

(1) $C_6H_5.SO_2Cl + H.OH \rightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5.SO_2OH} + HCl$

(2) $C_6H_5.SO_2Cl + C_2H_5OH \rightarrow \underset{\text{Ethyl benzene sulphonate}}{C_6H_5.SO_2.O.C_2H_5} + HCl$

(3) $C_6H_5.SO_2Cl + 2NH_3 \rightarrow \underset{\text{Benzene sulphonamide}}{C_6H_5.SO_2.NH_2} + NH_4Cl$

(4) $C_6H_5.SO_2Cl + \underset{\text{(Primary amine)}}{NH_2R} \rightarrow \underset{\text{Monalkyl benzene sulphonamide}}{C_6H_5.SO_2.NHR} + HCl$

(5) $C_6H_5.SO_2Cl + \underset{\text{(Secondary amine)}}{NH.R_2} \rightarrow \underset{\text{Dialkyl benzene sulphonamide}}{C_6H_5SO_2.NR_2} + HCl$

Reactions (4) and (5) form the basis of *Hinsberg's method* for the separation of the primary, secondary and tertiary amines (See Chap. 17 Sec. 5)

QUESTIONS

1. What do you understand by *sulphonation* ? How is the process carried out in the laboratory and on a large-scale ? To what use is it put in the manufacture of dyestuffs ?

2. Describe the chief physical and chemical properties of aromatic sulphonic acids.

3. How will you prepare a pure sample of benzene-sulphonic acid in the laboratory ? To what commercial use is the compound put ? How may it be converted into (*i*) benzene, (*ii*) phenol, and (*iii*) benzoic acid ?

4. What do you understand by the term *sulphonation* ? How will you transform benzene-sulphonic acid into (*a*) benzene, (*b*) phenol, and (*c*) benzoic acid ?
(Punjab, Inter., 1947)

5. (*a*) How is benzene-sulphonic acid obtained, and what is it used for ?
(*b*) Show what happens when benzene-sulphonic acid is treated with— (*i*) Phosphorus pentachloride, (*ii*) Superheated steam, and (*iii*) is fused with KOH.
(Punjab, Inter., 1940)

6. How is benzene sulphonic acid prepared, and how is it transformed into (*a*) benzene, (*b*) phenol, and (*c*) benzoic acid ? *(Punjab, Inter., 1941)*

7. Describe the preparation and properties of benzene-sulphonic acid ?
(Punjab, Inter., 1943)

CHAPTER 33

PHENOLS

1. Phenols are derived from aromatic hydrocarbons by the replacement of *nuclear* hydrogen by one or more hydroxyl groups. They are termed mono-, di-, or trihydric phenols according as one, two or three hydrogen atoms of the nucleus have been replaced.

Monohydric phenols are formed during the destructive distillation of wood and coal. Hence they are present in wood-tar and coal-tar. It is from the latter source that ordinary phenol (carbolic acid) and other mono-hydric phenols are commercially prepared.

2. General Methods of formation. Phenols may be prepared by the following general methods :—

(1) From *amino-compounds* by diazotization and warming the aqueous solution (*p.* 265),

(2) From *sulphonic acids* by fusion with alkalies (Chap. 32 Sec 2)

(3) From *halogen derivatives* of aromatic hydrocarbons *via* the Grignard reagents; *e.g.*,

$$\underset{\text{Bromobenzene}}{C_6H_5Br} \xrightarrow{+Mg} C_6H_5.Mg.Br \xrightarrow{+O_2} C_6H_5O.Mg.Br \xrightarrow{H.HO} \underset{\text{Phenol}}{C_6H_5OH}$$

(4) From a *phenolic acid* by heating with soda lime ; *e.g.*,

$$\underset{\text{Salicylic acid}}{C_6H_4(OH)COOH} + CaO \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + CaCO_3.$$

(5) From *lower homologues* by alkylation. This is effected by heating them with alcohols in the presence of zinc chloride; *e.g.*,

$$\underset{\text{Phenol}}{C_6H_5OH} + CH_3OH \rightarrow \underset{\text{o-and p-cresols}}{C_6H_4{<}^{CH_3}_{OH}} + H_2O$$

3. Physical Properties. The majority of phenols are colourless, crystalline substances, readily soluble in alcohol and ether. As a rule, solubility in water increases with the number of hydroxyl-groups in the molecule, while the volatility diminishes.

4. Reactions. The reactions of phenols may be discussed under three heads :

(*A*) *Those involving the Hydroxyl Group.* They are :—

(1) Phenols, like other hydroxy compounds react with phosphorus pentachloride :

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl.$$

(2) They react with acid anhydrides, yielding *esters*. Thus, when ordinary phenol is heated with acetic anhydride, it yields **phenyl acetate** (b. p. 195°), which is hydrolysed even by boiling water.

$$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}{>}O + C_6H_5OH \rightarrow \underset{\text{Phenyl acetate}}{CH_3COOC_6H_5} + CH_3COOH$$

(3) Phenols, like aliphatic alcohols, may be converted into *ethers* by heating their alkali salts with alkyl halides or with bromo derivatives of aromatic hydrocarbons, finely divided copper being used as a catalyst in the latter case.

$$C_6H_5.ONa + CH_3I \rightarrow C_6H_5O.CH_3 + NaI$$
Sodium phenate Methyl iodide Phenyl-methyl ether

$$C_6H_5ONa + C_6H_5Br \rightarrow C_6H_5.O.C_6H_5 + NaBr.$$
Diphenyl ether

(4) Owing to the combination of the hydroxyl group with the electro-negative benzene ring, phenols possess acidic properties, and dissolve in aqueous alkalies, yielding salts, such as sodium phenate, $C_6H_5.ONa$. They are, however, weakly acidic, and their salts with alkalies are decomposed by carbon dioxide (contrast salts of carboxylic acids). The dissolution of phenols in alkalies and reprecipitation by carbon dioxide is frequently made use of in the separation of phenols from neutral or more strongly acidic substances.

The acidic nature of phenols is influenced by the presence of other substituents in the ring. Thus, it is enhanced by the introduction of nitro groups.

(5) A characteristic reaction of phenols is that in aqueous or alcoholic solution they give a violet, green or yellow coloration with ferric chloride. Thus, ordinary phenol gives a violet, and carvacrol a green colour.

(6) When a phenol is heated with zinc-dust, it is reduced to the parent hydrocarbon.

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

(*B*) *Reactions involving Substitution in the Benzene ring.* The hydrogen atoms of the benzene ring in a phenol are more readily substituted than those of an aromatic hydrocarbon. Thus, ordinary phenol readily yields *s*-tribromophenol. $C_6H_2(OH)Br_3$, with bromine, *s*-trinitrophenol (picric acid). $C_6H_2(OH).(NO_2)_3$, with nitric acid.

(*C*) *Condensation Reactions.*

(1) Phenols in alkaline solution undergo coupling with diazonium salts, yielding azo-dyes (*p.* 267).

(2) Another important reaction of phenols is their condensation with phthalic anhydride. The products obtained are called **phthaleins.**

5. Tests of Phenols.

(1) *Reactions with Ferric Chloride.* [*See* Reaction (5) above].

(2) **Liebermann's Nitroso Reaction.** Most of the phenols, when warmed with concentrated sulphuric acid and a little sodium nitrite, give a dark-coloured product, which when added to water, produces a red colour. This, on the addition of an alkali, changes to intense blue or green. (*See* Expt 1, *p.* 277).

6. Distinguishing Characters of Phenols and Aliphatic Alcohols. Phenols differ from aliphatic alcohols in the following important points :

(1) They possess an acidic character.
(2) They give a violet, green or yellow colour with ferric chloride.
(3) They give Liebermann's nitroso reaction (Sec. 5 (2) above).
(4) They undergo coupling with diazonium compounds, yielding azo-dyes (*p.* 267).
(5) They undergo condensation with phthalic anhydride, yielding *phthaleins* (*p.* 274 Sec. 4)

7. Phenol, *Hydroxybenzene.* **Carbolic Acid,** C_6H_5OH. Phenol

is derived from benzene by the replacement of a hydrogen atom of benzene by a hydroxyl group :—

Benzene

Phenol

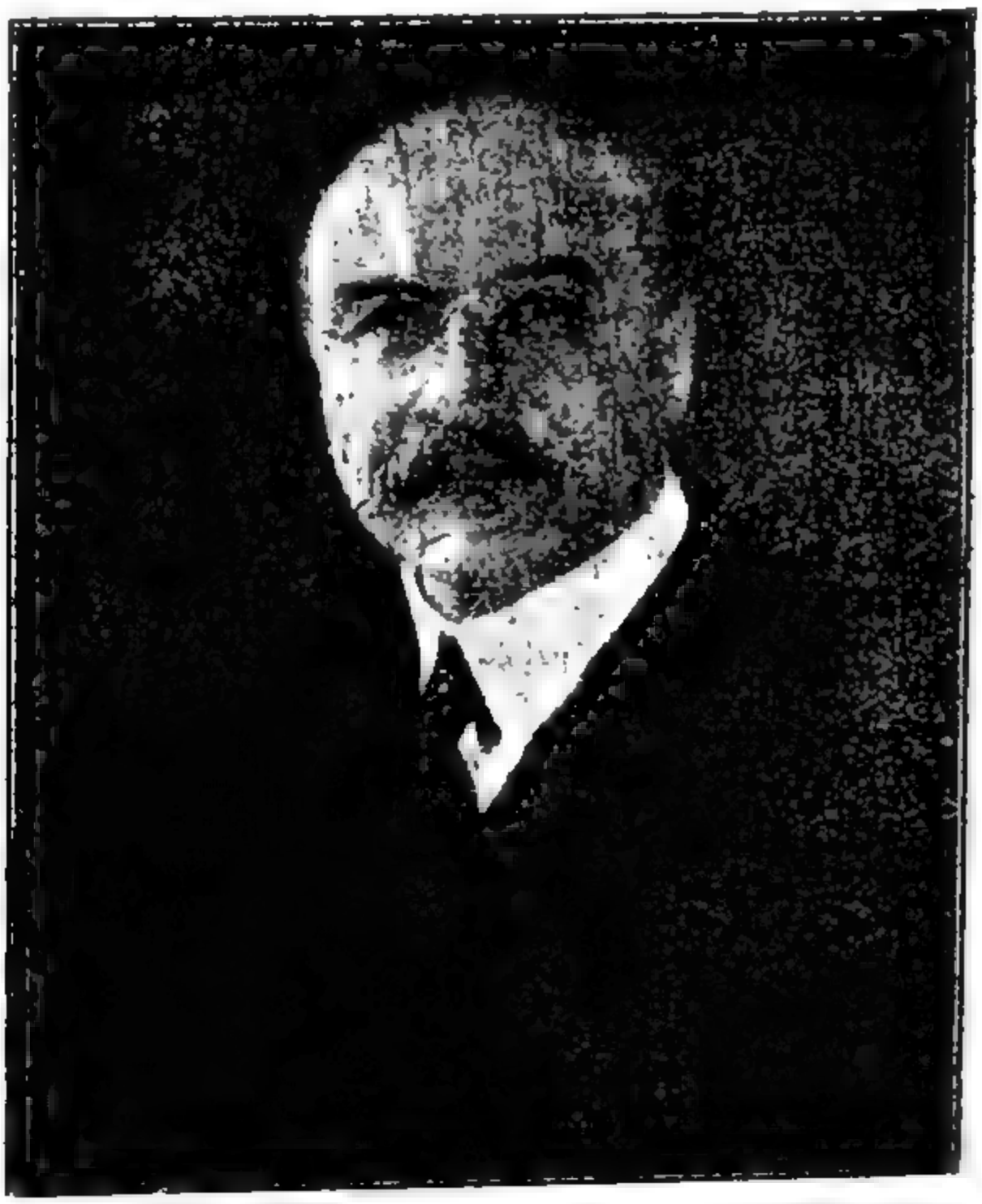
Occurrence. Phenol occurs in minute quantities, in the urine of man and that of the ox. It is the chief constituent of the "middle oil" fraction of the coal-tar distillation.

Preparation. (1) Phenol is mostly obtained from "middle oil" fraction of coal-tar distillation as described in Sec. 213.

(2) Some phenol of commerce is also prepared synthetically from benzene. The latter is converted into benzene-sulphonic acid, which is then fused with caustic soda.

Properties. When pure, phenol is a white, crystalline solid (m. p. 43°) which goes pink on exposure to air and light. It is deliquescent, and is liquefied on the addition of even a very small proportion of water. Phenol possesses a very characteristic odour, is highly poisonous, and has a strongly caustic action on the skin.

The most important **reactions** of phenol are :—



LEO HENDRIK BAKELAND (1863—).

A Belgian chemist, who, in 1889, migrated to America. He is well-known for his discovery of *bakelite* a resinous material used as an electrical insulator.

(1) *Acidic Character.* Phenol differs from aliphatic alcohols in shewing an acidic character, and dissolves alkalies, yielding salts that are stable in the presence of water :

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH \rightarrow \underset{\text{Sodium phenate}}{C_6H_5ONa} + H_2O$$

(2) *Reaction with Phosphorus Pentachloride.* Phenol, like other hydroxy compounds, reacts with phosphorus pentachloride, chlorobenzene being produced :—

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

(3) When heated with acetic anhydride, it gives phenyl acetate (*p.* 274).

(4) When added to a solution of ferric chloride, phenol gives a violet coloration.

(5) When heated with zinc-dust, phenol yields benzene :—

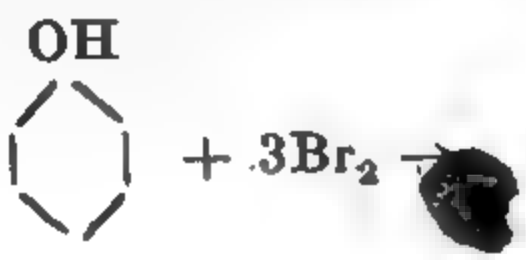
$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO.$$

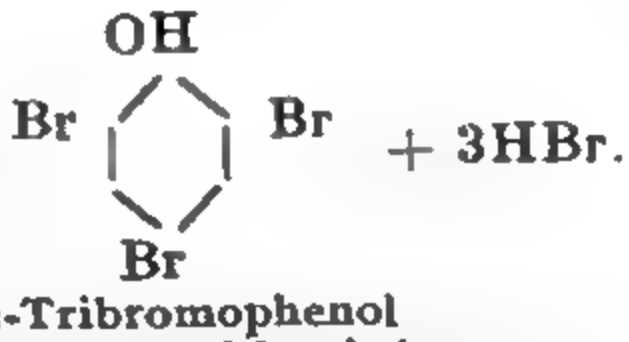
(6) **Liebermann's Nitroso Reaction.** See *p.* 275.

Expt. 1. Dissolve a little phenol in concentrated sulphuric acid, and add a piece of sodium nitrite. Pour the dark-coloured product into a beaker of cold water; a reddish liquid is formed. Now alkalify the liquid with sodium hydroxide; a bluish green solution results.

(7) *Reactions of the Benzene Nucleus.* Phenol also possesses the general reactions of the benzene nucleus. In fact the presence of the hydroxyl group in the nucleus renders the remaining nuclear hydrogen atoms readily replaceable by other substituents (compare aniline). The following reactions may be mentioned under this heading :—

(*i*) Chlorine and bromine give, even with an aqueous solution of phenol trihalogen derivatives ; *e.g* ,





s-Tribromophenol

(*ii*) Phenol is attacked by *dilute* nitric acid, giving *o*- and *p*- nitrophenols. With concentrated nitric acid it gives *s*-trinitrophenol or picric acid (*See* next section).

(*iii*) **Kolbe's Reaction.** When dry sodium phenate is heated with dry carbon dioxide in an autoclave at 140°, a carboxyl group is introduced into the nucleus at the *ortho*-position, producing the sodium derivative of salicylic acid (phenol-*o*-carboxylic acid) :—

Sodium phenate — Sodio-derivative of salicylic acid

The reaction is employed in the manufacture of salicylic acid.

Tests. Reactions (1), (4) and (6) given above may be employed in the identification of phenol.

Uses. (1) Phenol is used as a lotion for the dressing of wounds.

It is also employed for cauterizing the wounds caused by the bite of mad dog.

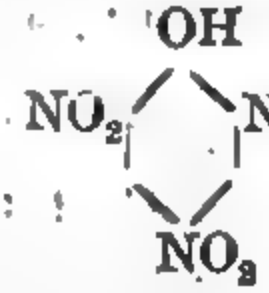
(2) In the manufacture of dyes.

(3) In making picric acid, which is used as an explosive.

(4) In the manufacture of certain medicinal chemicals such as salicylic acid, salol, aspirin, and phenacetin.

(5) A very important use of phenol is in the manufacture of **bakelite.** This is a resinous material obtained by the condensation of phenol and formaldehyde in the presence of catalysts, particularly ammonia. The chief use of bakelite is as an electrical insulator, but it also finds endless other applications where natural resins, celluloid or rubber are unsuited *e.g.*, pipe stems, handles aeroplane propellers, ornamental articles, varnishes, enamels, lacquers, and cement.

8. Picric Acid, 2 : 4 : 6-*Trinitrophenol*,



This important compound is prepared by the nitration of phenol. For this purpose, 1 part of phenol is dissolved in 4 parts of concentrated sulphuric acid, and the solution is added *gradually* to 8 parts of cold concentrated nitric acid. The temperature is kept at about 10° throughout the addition. At the end of the operation, the reaction mixture is gradually heated to 80°. The reaction proceeds with copious evolution of brown fumes of nitrogen dioxide. When no more fumes are coming off, the reaction mixture is allowed to cool. Crystals of picric acid separate out. They are removed from the mother liquor, washed with a little water, and finally purified by recrystallization from hot water.

Picric acid forms crystals of faint yellow colour having a bitter taste and melting at 122°. It dissolves in water to give a deep yellow solution. It is a fairly strong acid, and neutralizes alkalies, yielding yellow or red coloured salts.

The most valuable property of picric acid is that it explodes on detonation. For this reason, it is employed as a powerful explosive.

QUESTIONS

1. Describe the general methods for the preparation of phenols. What are the characteristic properties of these compounds? (*Punjab, Inter., 1938*)

2. Describe the commercial preparation of phenol from coal-tar. How does phenol react with, (*a*) sulphuric acid, (*b*) nitric acid, (*c*) sodium hydroxide, and (*d*) bromine? (*Punjab. Inter., 1941*)

3. Describe the important properties and uses of phenol.

4. State how you would proceed to introduce the hydroxyl-group into the benzene ring. (*Punjab, B. Sc., 1930*)

5. Write notes on :—(*a*) Kolbe's reaction, (*b*) Liebermann's nitroso reaction, and (*c*) bakelite.

6. How is picric acid prepared? What is it used for?

CHAPTER 34

AROMATIC ALCOHOLS, ALDEHYDES AND KETONES

1. Aromatic Alcohols. There are two classes of hydroxy derivatives of aromatic hydrocarbons, *viz*, (*i*) **phenols** in which the hydroxyl is in direct union with the benzene nucleus and (*ii*) **aromatic alcohols** which contain the hydroxyl group in the side chain. The former have been discussed in Chap. 33), and, as already seen, differ from aliphatic alcohols in several important respects. Aromatic alcohols, on the other hand, closely resemble aliphatic alcohols, in their methods of preparation and properties.

2. Benzyl Alcohol, $C_6H_5CH_2OH$. Benzyl alcohol is a typical example of an aromatic alcohol. It occurs as esters of benzoic and cinnamic acids in the balsams of Peru and Tolu and in storax.

Benzyl alcohol is usually prepared by the hydrolysis of benzyl chloride with an aqueous solution of potassium carbonate[1].

$$C_6H_5CH_2Cl + KOH \rightarrow C_6H_5CH_2OH + KCl$$

The benzyl chloride is boiled with potassium carbonate solution in a flask provided with a reflux condenser, until the pungent smell of the chloride has disappeared (6 to 8 hours). The benzyl alcohol is then extracted with ether and the etheral layer is separated, dried over anhydrous potassium carbonate and then distilled over a water bath to recover the ether. The distillation is then continued over wire-gauze, the water from the condenser being run off. The fraction passing at 200°—210° is collected separately.

Properties Benzyl alcohol is a colourless liquid having a faint, aromatic odour and is only sparingly soluble in water. It boils at 206°. In chemical properties, it closely resembles aliphatic primary alcohols, and forms ethers and esters When submitted to oxidation, it gives benzaldehyde $C_6H_5.CHO$, and finally benzoic acid, $C_6H_5.COOH$.

A point in which benzyl alcohol differs from the aliphatic alcohols is, that, when treated with sulphuric acid, it is resinified and not converted into the corresponding sulphuric ester.

Benzyl alcohol entirely lacks phenolic properties, and does not dissolve in alkalies, nor does it give any coloration with ferric chloride.

3. Aromatic Aldehydes. The aromatic aldehydes containing the aldehyde group in the nucleus are of far greater importance than those in which this group is present in the side-chain. They **differ from aliphatic aldehydes** in certain important particulars, as will be seen from the following account of benzaldehyde.

4. Benzaldehyde, CHO or $C_6H_5.CHO$.

Occurrence. Benzaldehyde occurs in bitter almonds as a glucoside called **amygdalin,** from which source it was formerly obtained ; hence the **name oil of bitter almonds**: Amygdalin is decomposed as follows by

---

[1]The alkali carbonates are hydrolysed in aqueous solution to give alkali hydroxide and carbonic acid,

$$K_2CO_2 + 2H.OH \rightleftharpoons 2KOH + H_2O + CO_2$$

The alkali hydroxide then hydrolyses the benzyl alcohol as shown above.

the hydrolytic action of the enzyme **emulsin**, also present in bitter almonds :—

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5.CHO} + HCN + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Methods of Formation. Benzaldehyde may be prepared by methods similar to those used for the preparation of aliphatic aldehydes; *e.g.*,

(1) By the oxidation of the corresponding primary alcohol, **benzyl alcohol** :—

$$\underset{\text{Benzyl alcohol}}{C_6H_5.CH_2OH} + O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5.CHO} + H_2O$$

(2) By distilling a mixture of calcium benzoate with calcium formate :—

$$\underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} + (HCOO)_2Ca \rightarrow \underset{\text{Benzaldehyde}}{2C_6H_5.CHO} + 2CaCO_3$$

(3) By reduction of benzoyl chloride (Rosenmund's method, page 120) :

$$\underset{\text{Benzoyl chloride}}{C_6H_5.COCl} + H_2 \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5.CHO} + HCl$$

(4) By the hydrolysis of benzal chloride with milk of lime :

$$\underset{\text{Benzal chloride}}{C_6H_5.CHCl_2} \xrightarrow{H.OH} \underset{\text{Unstable dihydroxy compound}}{C_6H_5.CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Benzaldehyde}}{C_6H_5.CHO}$$

In addition to the above methods, the following additional **methods**[1] may be used for the preparation of benzaldehyde :—

(1) *Direct introduction of the Aldehyde Group into the Benzene Ring* (**Friedel and Craft's reaction**). When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride, we get benzaldehyde. In this reaction formyl chloride, H.CO Cl, is produced as an intermediate product .—

$$CO + HCl \rightarrow \underset{\text{Formyl chloride}}{HCOCl}$$

$$\underset{\text{Benzene}}{C_6H_6} + HC\lessgtr^{Cl}_{O} \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

(2) *Oxidation of a Side-chain to a —CHO Group.* This may be effected in a number of ways :—

(i) **Etard's Reaction.** In this method toluene is oxidized by means of chromyl chloride. A solution of chromyl chloride in carbon disulphide is gradually added to toluene (also dissolved in carbon disulphide), when a dark-coloured precipitate consisting of an addition compound is obtained. This is separated by filtration and then decomposed by water, when benzaldehyde, chromic chloride and chromic acid are formed :—

$$C_6H_5CH_3 + 2CrO_2Cl_2 \rightarrow C_6H_5CH_3\,2CrO_2Cl_2$$
$$3CrO_2Cl_2 + H_2O \rightarrow 2CrCl_3 + H_2CrO_4 + 3O$$
$$C_6H_5CH_3 + 2O \rightarrow C_6H_5CHO + H_2O$$

The chromic acid is reduced by means of SO_2 and the mixture is then steam

[1] These methods are general ones for the preparation of aromatic aldehydes having the —CHO group in direct union with the benzene nucleus.

distilled. The benzaldehyde present in the distillate is extracted with ether. The ethereal layer is dried with calcium chloride : the ether passes over first and then benzaldehyde.

This method is the one usually employed for the **laboratory preparation** of benzaldehyde

(ii) By means of manganese dioxide and sulphuric acid in the presence of a little cupric sulphate as catalyst (See below, under Manufacture of Benzaldehyde).

Manufacture. Benzaldehyde is prepared on a large scale from toluene. Two different processes are in use :—

(1) *Through Benzal chloride* (*See p.* 247, Sec. 9).

(2) *By Direct Oxidation.* In the preparation of benzal chloride from toluene, no matter what preparations are taken, a small amount of chlorine enters the nucleus It is, therefore, impossible to prepare by the above process benzaldehyde free from chlorine. For use in perfumery, benzaldehyde must be of a high degree of purity. This is usually obtained by the direct oxidation of toluene with manganese dioxide and sulphuric acid in the presence of a small proportion of cupric sulphate as catalyser.

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + 2O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5.CHO} + H_2O.$$

Physical Properties. Benzaldehyde is a colourless, highly refractive liquid (b.p.179°) with a pleasant, characteristic odour, resembling that of bitter almonds. It is sparingly soluble in water, but is miscible with alcohol and ether in all proportions.

Reactions :—

(*A*) ***Resemblance with aliphatic aldehydes.*** Benzaldehyde resembles aliphatic aldehydes in the following respects :—

(1) It readily undergoes *oxidation*, even on exposure to air, yielding benzoic acid :—

$$C_6H_5CHO + O \rightarrow C_6H_5.COOH$$

It reduces ammoniacal silver solution (but not Fehling's solution).

(2) On *reduction*, it gives benzyl alcohol :—

$$C_6H_5.CHO + 2H \rightarrow C_6H_5.CH_2OH$$

(3) It reacts with *hydrogen cyanide* and *sodium bisulphite* to give a cyanohydrin and a bisulphite compound respectively.

(4) It also reacts with *hydroxylamine* and *phenylhydrazine* in exactly the same manner as the aliphatic aldehydes.

(5) It gives *Schiff's reaction* (*p.* 117).

(*B*) ***Distinction from Aliphatic Aldehydes.*** Benzaldehyde differs from aliphatic aldehydes in the following respects :—

(1) **Cannizzaro's Reaction.** When benzaldehyde is shaken with strong solution of sodium hydroxide, one molecule is oxidized at the expense of another with the formation of sodium benzoate and benzyl alcohol (compare Formaldehyde, *p.* 119).

$$2C_6H_5.CHO + NaOH \rightarrow C_6H_5.COONa + C_6H_5.CH_2OH.$$

(2) *Reaction with Ammonia.* When treated with ammonia, benzaldehyde forms **hydrobenzamide,**

$$3C_6H_5.CHO + 2NH_3 \rightarrow (C_6H_5.CH)_3N_2 + 3H_2O$$

(3) **Benzoin condensation** When benzaldehyde is warmed with an alcoholic solution of potassium cyanide' two molecules condense together to f rm a keto-alcohol, called *benzoin* :

$$C_6H_5CH{=}O \quad + \quad H.CO.C_6H_5 \rightarrow \underset{\text{Benzoin}}{C_6H_5CH(OH).CO.C_6H_5}$$

(4) Benzaldehyde condenses with certain alphatic and aromatic compounds with the elimination of water, yielding *unsaturated* products ; *e g*.,

(*a*) $$C_6H_5.CHO + \underset{\text{Aniline}}{H_2NC_6H_5} \xrightarrow{\text{Heat}} \underset{\text{Benzylidene-aniline}}{C_6H_5CH{:}N.C_6H_5} + H_2O$$

(*b*) $$C_6H_5.CHO + \underset{\text{Acetaldehyde}}{H_2.CH.CHO} \rightarrow \underset{\text{Cinnamaldehyde}}{C_6H_5CH{:}CH.CHO} + H_2O$$

(*c*) $$C_6H_5.CHO + \underset{\text{Sodium acetate}}{H_2CH.COONa} \rightarrow \underset{\text{Sodium cinnamate}}{C_6H_5.CH{:}CH.COONa} + H_2O$$

Reaction (*b*) known as **Claisen's reaction**, is brought about in the prese ice of a trace of alkali Reaction (*c*) called **Perkin's reaction,** is affected by h eating the substance with acetic anhydride, which serves to take up water.

(5) Benzaldehyde may be nitrated and sulphonated, the *meta*-compounds being th e p incipal produc's. Chlorination of benzaldehyde leaves the nucleus unaffected, the chlorine replacing the hydrogen of the aldehydic group with the production of benzoyl chloride :—

$$C_6H_5CHO + Cl_2 \rightarrow C_6H_5.COCl + HCl$$

The reaction is employed in the commercial preparation of benzyl chloride

Tests. 1. Bnzaldehyde has the smell of oil of bitter almonds.

2. On warming 0 5 c.c of the aldehyde with 0 5 c.c. of aniline and a pinch of fused zinc chloride and cooling, a white solid is deposited.

3. On heating a mixture of the aldehyde, dimethylaniline and fused zinc chloride, a deep green coloration is developed.

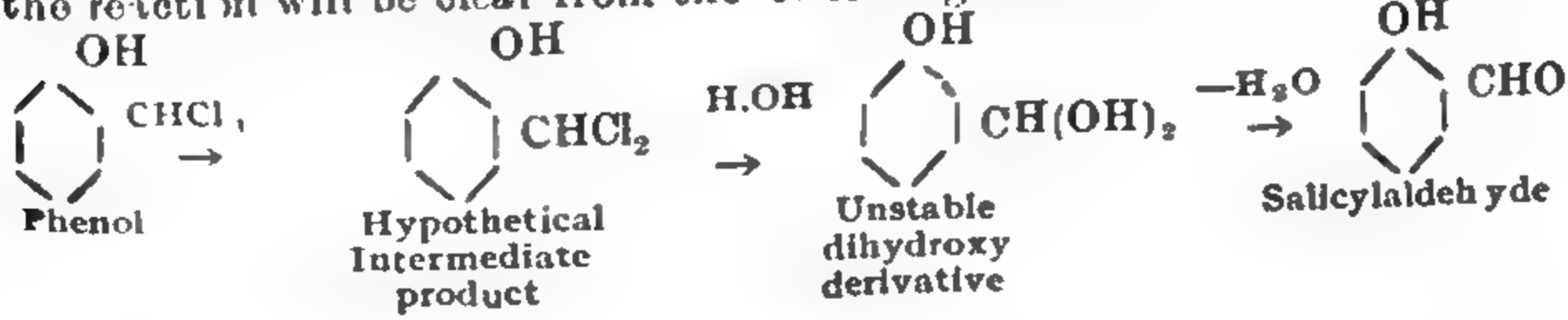
Uses. Benzaldehyde is used:—

(*i*) In perfumery.

(*ii*) In the manufacture of dyes

5 Salicylaldehyde, *o-Hydroxybenzaldehyde*,

This compound is prepared from phenol by the **Reimer-Tiemann reaction** which involves the *direct introduction of an aldehyde group* into the phenol molecule. The reaction is carried out by heating a strongly alkaline solution of phenol with chloroform. Along with the aldehyde, its isomer, *p*-hydroxybenzaldehyde, is also produced. These two products are separated from each other by acidifying the reaction mixture and steam distilling, *p*-isomer being non-volatile The mechanism of the reaction will be clear from the following scheme :—



Salicylaldehyde is an oily liquid boiling at 196° and having a penetrating; nitrobenzene-like odour It colours the skin yellow. Salicylaldehyde possesses the properties of a phenol and of an aldehyde. Like phenol itself, salicylaldehyde gives a violet colour with ferric chloride When submitted to oxidation it is converted to salicylic acid, $C_6H_4(OH)COOH$; and when reduced with sodium amalgam it yields **salicyl alcohol,** $C_6H_4 < {OH \atop CH_2OH}$ (compare acetaldehyde).

Tests. 1. Salicylaldehyde smells like oil of mirbane.
2. It colours the skin yellow
3. It is freely soluble in sodium hydroxide.
4. It gives violet coloration with ferric chloride solution.

6. Aromatic Ketones. There exist (*i*) purely aromatic ketones, such as benzophenone, $C_6H_5CO.C_6H_5$, and (*ii*) mixed alphyl-aryl ketones ,*e.g.*, acetophenone, $C_6H_5.CO.CH_3$. Both the classes closely resemble the aliphatic ketones in their properties.

2. Aromatic ketones may be prepared by methods similar to those used for aliphatic ketones (p. 113 Sec. 2), and also by the interaction of benzene hydrocarbons and acid chlorides in the presence of anhydrous aluminium chloride (**Friedel and Crafts' reaction**) *e.g.*.

$$C_6H_6 + \underset{\text{Benzoyl chloride}}{Cl.CO.C_6H_5} \rightarrow \underset{\text{Benzophenone}}{C_6H_5.CO\,C_6H_5} + HCl$$

7. Acetophenone, *phenyl-methyl Ketone.* $C_6H_5.CO.CH_3$ This is the best known of the alphyl-aryl ketones. It may be prepared—

(*i*) By distilling an equimolecular mixture of calcium benzoate and calcium acetate :

$$(C_6H_5.COO)_2Ca + (CH_3COO)_2Ca \rightarrow 2C_6H_5.CO.CH_3 + 2CaCO_3$$

(*ii*) By dropping acetyl chloride into well-cooled benzene in the presence of anhydrous aluminium chloride (*Friedel and Crafts' reaction*):

$$C_6H_6 + Cl.CO.CH_3 \rightarrow C_6H_5.CO.CH_3 + HCl.$$

Properties. Acetophenone is a crystalline solid (m. p.20°, b. p. 202°) having a fragrant odour. It is slightly soluble in water.

In chemical behaviour, acetophenone is very similar to acetone.

Thus, on reduction with sodium amalgam and aqueous alcohol it yields the secondary alcohol *methyl phenyl carbinol.*

$$C_6H_5.CO.CH_3 + 2H \rightarrow C_6H_5.CHOH.CH_3.$$

On oxidation, the aliphatic side-chain gets oxidized to a carboxyl group with the production of benzoic acid :

$$C_6H_5.CO.CH_3 + 4O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + CO_2 + H_2O$$

Further, it reacts with hydrogen cyanide, hydroxylamine and phenylhydrazine in exactly the same manner as aliphatic ketones.

However, acetophenone *does not combine with sodium bisulphite.* This is characteristic of all ketones in which the carbonyl group is in direct combination with the benzene ring.

Acetophenone, of course, differs from aliphatic ketones in the fact that, as an aromatic compound, it can be nitrated and sulphonated.

Tests. The following facts about acetophenone may be used to identify this substance :—

1. Its melting point (20°) and insolubility in water.
2. On oxidation with alkaline permanganate, it gives Benzoic acid, which melts at 121°, and may be further identified by tests desoribed (on page 287)
3. It forms an oxime (m.p. 59°) and a phenylhydrazone (m. p. 105°.)

Use. Acetophenone is used as a *hypnotic* in medicine, under the name of hypnone.

8. **Benzophenone**, *Diphenyl Ketone*. $C_6H_5.CO.C_6H_5$. This compound is best prepared from benzene by Friedel and Crafts' reaction.

$$C_6H_6 + \underset{\text{Benzoyl chloride}}{C_6H_5.COCl} \rightarrow C_6H_5.CO.C_6H_5 + HCl$$

$$2C_6H_6 + \underset{\text{Carbonyl chloride}}{COCl_2} \rightarrow C_6H_5.CO.C_6H_5 + 2HCl$$

Benzophenone forms colourless crystals (m. p. 48°). It possesses the usual properties of a ketone, and reacts with hydrogen cyanide, hydroxylamine, and phenylhydrazine etc., in exactly the same manner as aliphatic ketones. When subjected to reduction it first gives the secondary alcohol, diphenyl carbinol, $(C_6H_5)_2CHOH$, and then diphenyl methane, $(C_6H_5)_2CH_2$. The first stage of reduction is effected by means of sodium amalgam and the socond by distillation with zinc-dust.

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!CO \xrightarrow{\text{Na-amalgam}} \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!CHOH \xrightarrow[\text{Zn-dust}]{\text{Distil with}} \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!CH_2$$

Tests. Benzophenone may be identified by means of the following properties of this compound :—

1. Its melting point (48°), boiling point (305°) and insolubility in water.
2. Dissolves in concentrated sulphuric acid to form a yellow solution.
3. When fused with KOH, it yields benzoic acid (m. p. 121°) and benzene (b.p. 80°).
4. Its oxime melts at 141° and phenylhydrazone at 137°.

QUESTIONS

1. Describe the preparation and properties of benzyl alcohol. In what important respects does it differ from phenol ?
2. How is benzaldehyde prepared ? Describe the action on this compound of (*a*) potassium hydroxide, (*b*) ammonia, (*c*) nitric acid. Give equations. (*Punjab. Inter., 1922*)
3. In what important respects do benzaldehyde and acetaldehyde differ from and resemble each other ?
4. How is benzaldehyde prepared on a commercial scale ? What uses is it put to ?
5. Describe the preparation, properties and uses of acetophenone. (*Punjab, Inter., 1942*)
6. Write notes on : (*a*) Friedel and Crafts' reaction. (*b*) Etard's reaction. (*c*) Cannizzaro's reaction, and (*d*) Benzoin condensation.

CHAPTER 35

AROMATIC ACIDS

1. General Methods of Preparation The aromatic acids may be obtained by the usual methods for preparing aliphatic carboxylic acids ; *e.g.* :—

(1) *By the Oxidation of a Primary Alcohol or an Aldehyde* :—

$$\underset{\text{Benzyl alcohol}}{C_6H_5.CH_2OH} + 2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5.CHO} + O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(2) *By the Hydrolysis of a Nitrile* :—

$$\underset{\substack{\text{Benzo-nitrile}\\ \text{(Phenyl cyanide)}}}{C_6H_5.CN} + 2H_2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5.COOH} + NH_3$$

In addition to the above, the following additional methods are available for preparing the aromatic acids containing the —COOH group in direct union with the benzene nucleus :—

(1) *Direct Introduction of the Carboxyl Group into the Benzene nucleus* (Friedel and Crafts' reaction). When a benzene hydro-carbon is treated with carbonyl chloride in the presence of anhydrous aluminium chloride, we get an acid chloride, which, on treatment with water, gives the corresponding acid ; *e.g.*

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Carbonyl chloride}}{Cl.CO.Cl} \rightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

$$C_6H_5COCl + H_2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl$$

(2) *By Oxidation of a Side-chain.* The oxidation of a homologue of benzene (or of a derivation containing a substituted side-chain) is the most important method of preparing aromatic acids, The aliphatic side-chain, whatever its length, is oxidized to carboxyl group. The oxidation is effected by means of dilute nitric acid, or potassium permanganate in alkaline solution.

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + 3O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5.COOH} + H_2O$$

(3) *From an Amino Compound through Sandmeyer's Reaction* :

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{\text{Diazotize}} \underset{\substack{\text{Benzene}\\ \text{diazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} \xrightarrow{CuCN} \underset{\text{Benzonitrile}}{C_6H_5CN} \xrightarrow{H.OH} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(4) *From a Sulphonic Acid.* When the potassium salt of an aromatic sulphonic acid is fused with potassium cyanide, we get a nitrile, which, on hydrolysis, gives an acid ; *e.g.*,

$$\underset{\substack{\text{Potassium benzene}\\ \text{sulphonate}}}{C_6H_5SO_2OK} \xrightarrow{KCN} \underset{\text{Benzo-nitrile}}{C_6H_5CN} \xrightarrow{H.OH} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

2. General Properties. Aromatic carboxylic acids are colourless, crystalline solids, readily soluble in hot water, less so in the cold. In

chemical behaviour they resemble the aliphatic acids. On account of the electronegative nature of the benzene nucleus, the aromatic acids are stronger than the aliphatic acids. Further, like aromatic hydrocarbons, they may be converted into the chloro, nitro, amino and other derivatives.

3. Benzoic Acid. COOH, or $C_6H_5.COOH$.

Occurrence. (1) Benzoic acid occurs in the free state in gum benzoin and in the balsams of Peru and Tolu.

(2) In the form of hippuric acid (benzoylglycine, $C_6H_5CO.NH.CH_2.COOH$), it is present in the urine of the horse

Preparation. (1) Benzoic acid is obtained on the commercial scale from toluene. The latter substance is first chlorinated at its boiling-point to get benzotrichloride, which is then hydrolysed with milk of lime.

$$C_6H_5.CH_3 + 3Cl_2 \rightarrow \underset{\text{Benzotrichloride}}{C_6H_5CCl_3} + 3HCl$$

$$C_6H_5CCl_3 \xrightarrow{H.OH} \underset{\text{(Unstable)}}{C_6H_5.C(OH)_3} \xrightarrow{-H_2O} \underset{\text{Benzoic acid}}{C_6H_5.COOH}$$

The calcium salt of benzoic acid, thus obtained is treated with hydrochloric acid, when benzoic acid is precipitated. The acid is purified by crystallization from hot water.

(2) Much benzoic acid is also prepared commercially from naphthalene *via* phthalic acid (Sec 294). The latter substance is partially decarboxylated by cautiously heating with soda-lime :—

$$C_6H_4{<}\begin{matrix}COONa\\COONa\end{matrix} + NaOH \rightarrow C_6H_5COONa + Na_2CO_3$$

(3) In the laboratory the acid is usually obtained by the oxidation of benzyl chloride, $C_6H_5CH_2Cl$, by means of an alkaline solution of potassium permanganate. Benzyl chloride is probably first hydrolysed by the alkali into benzyl alcohol, which is then oxidized by potassium permanganate to benzoic acid :

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + H.OH \rightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + HCl$$

$$C_6H_5CH_2OH + 2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

Expt. 1. Preparation of Benzoic Acid. In a round-bottom, one-litre flask provided with a reflux condenser (Fig. 1) are placed benzyl chloride (1 part) and a solution of Na_2CO_3 (1 part) in water (10 parts). The mixture is gently boiled, and the calculated amount of potassium permanganate (1·8 parts) dissolved in water (30 parts) is added gradually from a dropping funnel pushed down the top of the condenser. The boiling is continued, until the pink colour of the permanganate has disappeared. The liquid is allowed to cool to about 80°, and a current of sulphur dioxide is passed into it, until the precipitate of manganese dioxide has completely dissolved. On allowing the reaction mixture to cool, crystals of benzoic acid separate out. These are filtered off,

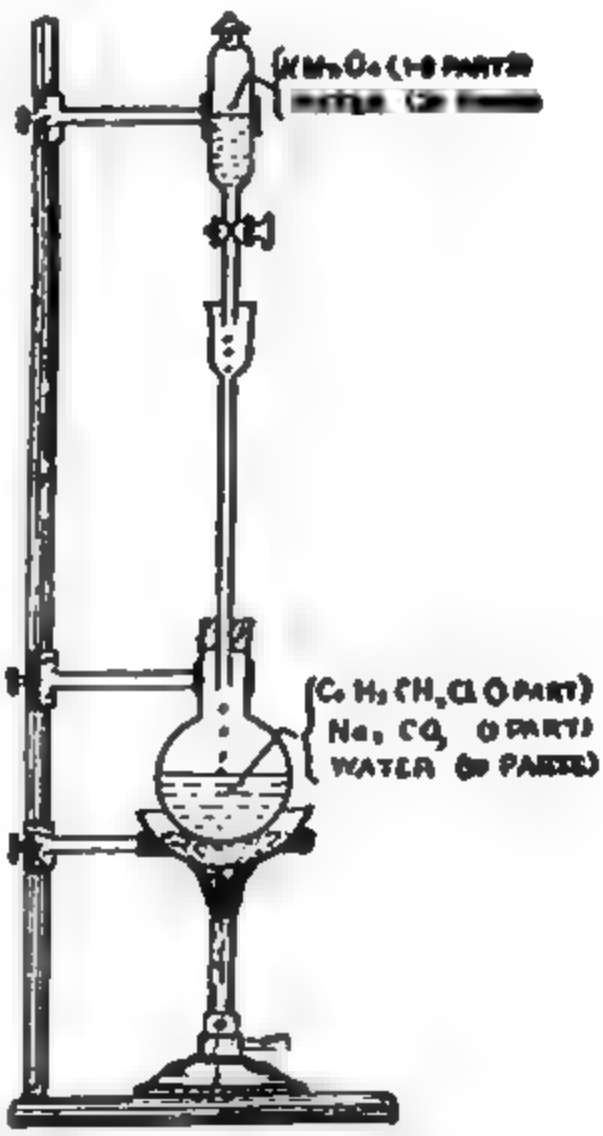


Fig. 1. Preparation of Benzoic Acid from Benzyl Chloride.

washed with a small quantity of cold water, and finally recrystallized from hot water.

(3) For pharmaceutical purposes, benzoic acid is still obtained from gum benzoin by sublimation.

Physical Properties. Benzoic acid forms colourless, glistening plates (m.p 121°, b.p. 250°), and has a faint aromatic odour. It is readily soluble in hot water, alcohol and ether. It sublimes readily and is volatile in steam; the vapour has an irritating action on the nose and throat, and causes violent coughing.

Reactions. In chemical behaviour, benzoic acid closely resembles acetic acid.

(1) It forms salts and esters just as acetic acid and other carboxylic acids do :—

$$C_6H_5COOH + NaOH \rightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + H_2O$$

$$C_6H_5COOH + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + H_2O$$

(2) When treated with phosphorus pentachloride, it gives benzoyl chloride :—

$$C_6H_5COOH + PCl_5 \rightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + POCl_3 + HCl$$

(3) When benzoyl chloride and sodium benzoate are allowed to react together, they give benzoic anhydride:

$$\begin{matrix} C_6H_5COCl \\ + \\ C_6H_5.COONa \end{matrix} \rightarrow \underset{\text{Benzoic anhydride}}{\begin{matrix} C_6H_5CO \\ \\ C_6H_5CO \end{matrix}\!\!>\!O} + NaCl$$

(4) When the sodium salt of benzoic acid (or the acid itself) is distilled with soda-lime, benzene is produced :—

$$C_6H_5COONa + NaOH \rightarrow \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

(5) Like other aromatic compounds, benzoic acid may be nitrated or sulphonated.

Tests Benzoic acid and its salts may be identified by the tests described in the following experiment.

Uses. Benzoic acid is used :—

(*i*) In medicine, and
(*ii*) in the manufacture of dyes.

4. Benzoyl Chloride, $C_6H_5.COCl$, is obtained by distilling benzoic acid with phosphorus pentachloride :—

$$C_6H_5.COOH + PCl_5 \rightarrow C_6H_5.COCl + POCl_3 + HCl$$

It is also prepared commercially from benzal chloride. The latter substance on hydrolysis yields benzaldehyde, which on chlorination gives benzoyl chloride (page 355) :—

$$C_6H_5.CHCl_2 + 2H.OH \rightarrow C_6H_5.CHO + 2HCl$$
$$C_6H_5.CHO + Cl_2 \rightarrow C_6H_5.COCl + HCl$$

Benzoyl chloride is a colourless, oily liquid with an extremely irritating colour. In the ohemical behaviour, benzoyl chloride is analogous to acetyl chloride. Thus, it is decomposed by water, though far more slowly than acetyl chloride, yielding benzoic acid and hydrochloric acid.

$$C_6H_5.COCl + H.OH \rightarrow C_6H_5.COOH + HCl$$

Use. Benzoyl chloride is frequently employed for introducing the benzoyl group, $C_6H_5CO—$, into hydroxy and amino compounds. The process is known as **benzoylation**, and is carried out by shaking the compound to be benzoylated with an excess of benzoyl chloride and dilute sodium hydroxide solution **(Schotten-Baumann reaction)**

$$\underset{\text{Phenol}}{C_6H_5OH} + Cl.CO\,C_6H_5 \rightleftharpoons \underset{\text{Phenyl benzoate}}{C_6H_5COO.C_6H_5} + HCl$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + C_6H_5COCl \rightleftharpoons \underset{\text{Benzanilide}}{C_6H_5CO.NH.C_6H_5} + HCl$$

The alkali serves to remove the hydrochloric acid as soon as formed, and thus prevents the reaction from being reversed. The benzoyl derivative is separated by filtration or extraction with ether, and is then purified. Since benzoyl derivatives crystallize much more readily than the correspondig acetyl derivatives, they are prepared in preference to the latter for the *identification or isolation of hydrory and amino compounds.*

Expt. 3 Benzoylation of Aniline :—

Aniline, 2 gm.

Benzoyl chloride, 2 c.c.

Place aniline[1] and sodium hydroxide solution in a small flask, and warm the latter on a water-bath. Add benzoyl chloride gradually to the warm mixture with continuous shaking. Loosely cork the flask, and shake the contents as vigorously as possible for a few minutes. If the smell of benzoyl chloride still persists, destroy it by warming it with a further quantity of sodium hydroxide solution. Pour the contents of the flask into water, when benzanilide, $C_6H_5.NH.CO.C_6H_5$ will separate out as a precipitate. Filter the precipitate, wash with water, dry and recrystallize from alcohol (M. P. 161—162°).

5. Benzoic Anhydride, $(C_6H_5CO)_2O$. This compound is prepared by the interaction of benzoyl chloride and sodium benzoate (compare acetic anhydride).

$$\begin{matrix} C_6H_5CO.\ \ Cl \\ + \\ C_6H_5.COO\ Na \end{matrix} \rightarrow \begin{matrix} C_6H_5.CO \\ \\ C_6H_5.CO \end{matrix}\!\!>\!O + NaCl$$

It is a crystalline substance, closely resembling acetic anhydride in its chemical behaviour. Like benzoyl chloride, the anhydride is also employed for the *benzoylation* of hydroxy and amino compounds.

6. Benzamide, $C_6H_5CONH_2$ The amide of benzoic acid is obtained by the action of ammonium carbonate on benzoyl chloride or ethyl benzoate :—

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + NH_3 \rightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl$$

$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + NH_3 \rightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + C_2H_5OH$$

Expt. 4. *Preparation of Benzamide.*—

[1] If the compound to be benzoylated is a solid, it should be *finely powdered* beforehand.

Ammonium carbonate, 10 gm.
Benzoyl chloride, 5 gm. (4 c.c.)

Place the finely powdered ammonium carbonate in a mortar, add benzoyl chloride from a burette, and thoroughly rub the mixture with a pestle. If the smell of benzoyl chloride persists even after 10 minutes, add a few drops of concentrated ammonia to complete the reaction. Treat the product with water to dissolve out the ammonium chloride. Filter the solid benzamide at the pump, and wash with *cold* water. Recrystallize from hot water, and dry the crystals on a porous plate.

Benzamide is a colourless, crystalline solid, readily soluble in hot water. It is similar to acetamide in its chemical properties, and, when boiled with alkalies, it gives ammonia and the alkali benzoate

$$\underset{\text{Benzamide}}{C_6H_5.CONH_2} + KOH \rightarrow \underset{\text{Potassium benzoate}}{C_6H_5COOK} + NH_3$$

7. Ethyl Benzoate. $C_6H_5.COOC_2H_5$. Ethyl Benzoate is prepared by the **Fischer-Speier method.** This consists in boiling benzoic acid with twice its weight of absolute alcohol in the presence of a little concentrated sulphuric acid or anhydrous hydrogen chloride, which act as catalysts.

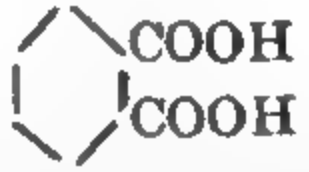
$$C_6H_5.COOH + C_2H_5OH \rightleftharpoons C_6H_5COOC_2H_5 + H_2O.$$

Expt. 5. *Preparation of Ethyl Benzoate.*—
Benzoic acid 50 gm.
Absolute alcohol, 100 gm. (125 c. c.)
Concentrated Sulphuric acid, 10 gm. (5.4 c. c.)

Place the mixture in a round-bottom flask provided with a reflux condenser, and boil it for 3 hours. Distil off the greater part of alcohol and pour the residue into about 5 times its volume of cold water. Neutralize the liquid with solid sodium carbonate, and extract the oily ester with ether. Separate the ethereal layer and dry it over fused calcium chloride. Decant the clear liquid, into a distillation flask and distil off the ether. Replace the water condenser by an air condenser; and distil off ethyl benzoate, catching the fraction passing over at 205-215° in a clean dry receiver.

Ethyl benzoate has a pleasant, aromatic odour, and boils at 213°. It closely resembles ethyl acetate in its chemical properties. Thus, when boiled with alcoholic potash, it gets hydrolysed into ethyl alcohol and potassium benzoate :—

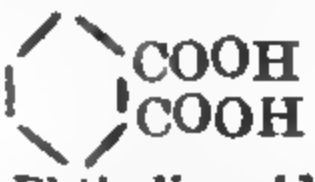
$$\underset{\text{Ethyl benzoate}}{C_6H_5.COOC_2H_5} + KOH \rightarrow \underset{\text{Potassium benzoate}}{C_6H_5COOK} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

8. Phthalic Acid,  , or *Benzene-o-dicarboxylic Acid.*

Preparation. This acid may be obtained by the oxidation of *o*-xylene and other benzene derivatives containing two aliphatic side chains in the *ortho*-position. It is technically prepared on a very large scale by the oxidation of naphthalene with fuming sulphuric acid in the presence of mercuric sulphate, which acts as a catalyser :

Naphthalene

$$+ 9O \rightarrow$$


Phthalic acid

$$+ 2CO_2 + H_2O$$

During the oxidation, the SO_3, present in the acid gets reduced to SO_2.

A more recent commercial process devised by Wohl and Gibbs consists in passing a mixture of naphthalene vapour and air over vanadium pentoxide heated at about 400°. The product consists of phthalic anhydride.

Properties. Phthalic acid is a colourless, crystalline substance which melts at 184°, yielding the anhydride :

$$C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+H_2O$$

Phthalic anhydride

If the melted substance be allowed to solidify and its melting point redetermined, it will be found to be 128°, the melting-point of the anhydride.

Phthalic anhydride sublimes readily, yielding long, needle-shaped crystals. It slowly combines with water, regenerating phthalic acid. When heated in a current of ammonia, it yields **Phthalimide** :—

$$C_6H_4\begin{matrix}CO\\CO\end{matrix}>O+NH_3 \rightarrow C_6H_4\begin{matrix}CO\\CO\end{matrix}>NH+H_2O,$$

which when treated with alcoholic potash yields a **potassium phthalimide,**

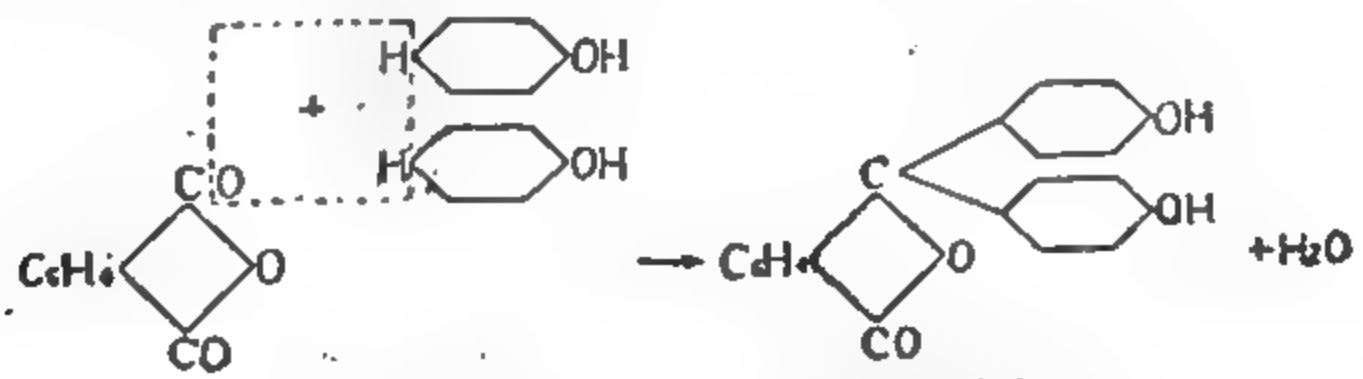
$$C_6H_4\begin{matrix}CO\\CO\end{matrix}>NK$$

Test. Both phthalic acid and the anhydride can be readily identified by the **fluorescein reaction.**

Expt. 6. *Fluorescein Reaction.* Heat strongly a mixture of resorcinol and phthalic anhydride in a test tube. Dissolve the product in aqueous sodium hydroxide. A brownish red solution is obtained which, when poured into a large volume of water, shows a magnificent green fluorescence.

Uses. Phthalic acid is used in the preparation of over 200 compounds. Its most important commercial use is in the manufacture of indigo and of the dyes known as *phthaleins.*

9. Reaction of Phthalic Acid with Phenols. An important class of dyes, called **phthaleins,** is obtained by the condensation of phthalic anhydride with the *para* hydrogen of phenols. The simplest example is **phenolphthalein,** which is obtained by heating phthalic anhydride with phenol at 120° in the presence of concentrated sulphuric acid (catalyst) :—



Phenolphthalein

Expt. 7. Take about 2 gm. of phthalic anhydride, 4 gm. of phenol, and 1 ml. of concentrated sulphuric acid in a test tube. Heat the mixture at 115-120° for a short time. Allow to cool somewhat, and pour the product into a beaker full of water. Alkalify with sodium hydroxide : a pink colour is developed, which on the addition of acid, gets discharged.

Phenolphthalein is a white, crystalline substance, melting at 250°. It is readily soluble in alcohol but insoluble in water. It is colourless in acid and neutral solutions, but acquires an intense rose-red colour in the presence of alkali.

Phenolphthalein is used as a laxative, and as an indicator in the titration of strong alkalis. It is not used as a dye.

Another important member of this class is **fluorescein** which is obtained by heating resorcinol with phthalic anhydride at 200°. It is an orange powder slightly soluble in water, but dissolves in the presence of alkali to give a brilliant **green-red fluoresence.**

Expt. 8. Heat a mixture of resorcinol, phthalic anhydride and concentrated sulphuric acid in a test-tube. Dissolve the product in aqueous sodium hydroxide. A brownish-red solution is obtained, which, when poured in a large volume of water in a beaker, shows a magnificent green fluorescence.

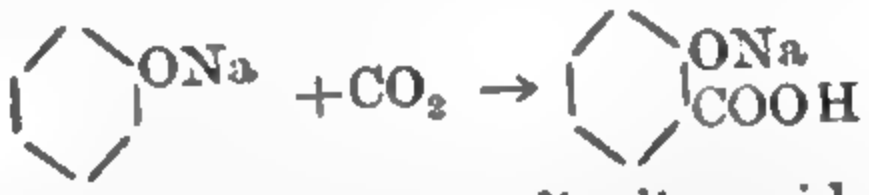
Eosine, the tetrabromo derivative of fluorescein, is a red powder soluble in alcohol. Its disodium or ammonium salt is used as a direct dye for silk and for staining biological specimens. A dilute solution of the salt is used as **red-ink**.

10 Phenolic Acids. These are derived from the aromatic carboxylic acids by the substitution of the *nuclear* hydrogen by one or more hydroxyl groups The phenolic acids have the dual character of a phenol and a carboxylic acid.

11. Salicylic Acid, *o-Hydroxy-benzoic Acid.*

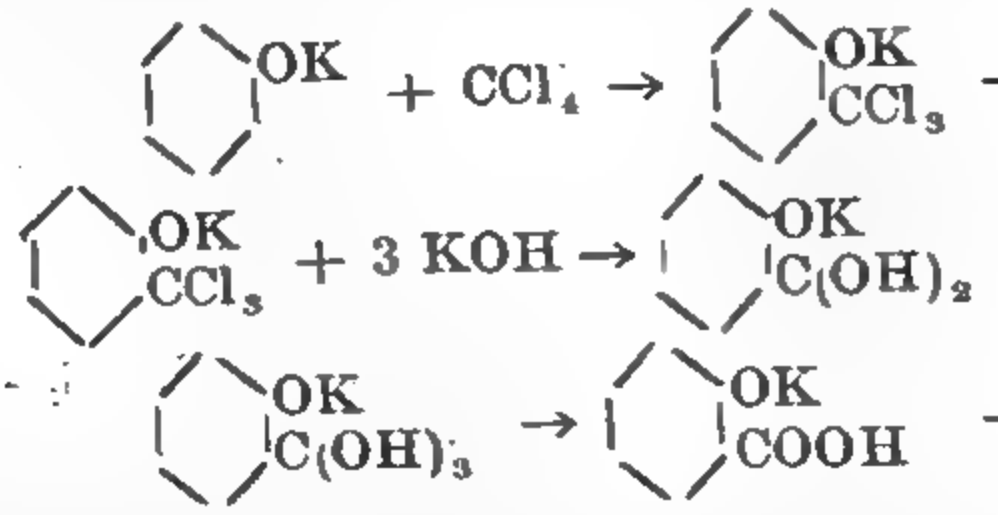
Occurrence. The acid occurs as the methyl ester in the oil of wintergreen (*Gaultharia procumbens*), from which source the acid employed in pharmacy was formerly obtained. Sweet birch oil also consists almost entirely of methyl salicylate.

(1) **Preparation.** *From Phenol by Kolbe's Reaction.* Salicylic acid is prepared on a large scale from phenol by **Kolbe's process.** Dry sodium phenate, C_6H_5ONa, is heated with dry carbon dioxide in an autoclave at 140°. The carbon dioxide enters the nucleus in the *ortho*-position, producing the sodio-derivative of phenyl-*o*-carboxylic acid :—



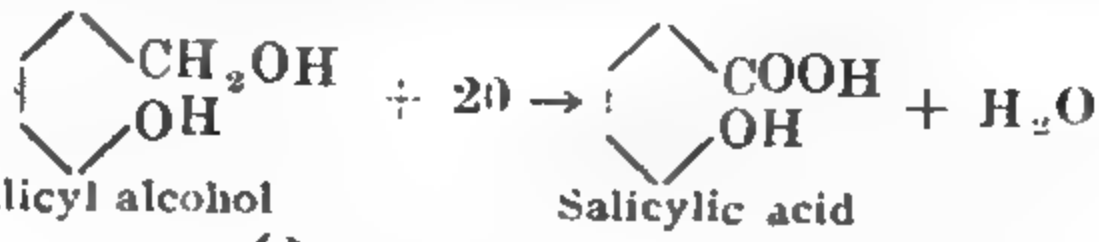
From the reaction product free salicylic acid is precipitated by the addition of hydrochloric acid, and is purified by recystallization from hot water.

(2) *From Phenol by the action of Carbon Tetrachlroide.* When a strongly alkaline solution of phenol is boiled with carbon tetrachloride, salicylic acid[1] is produced. The reaction may be supposed to occur in the following steps :—

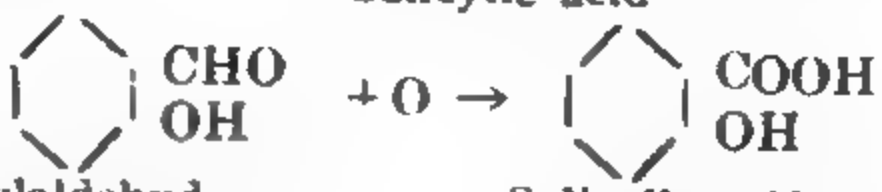


[1] At the same time, some p-hydroxy-benzoic acid is also formed.

(3) *By the Oxidation of Salicyl Alcohol or Salicylaldehyde.* This is effected by means of chromic acid.



Salicyl alcohol — Salicylic acid



Salicylaldehyde — Salicylic acid

(4) *From o-Aminobenzoic Acid.* The acid is first diazotized and the product is boiled with water :—

o-Aminobenzoic acid — Diazonium salt — Salicylic acid

Physical Properties. Salicylic acid forms colourless needles (m. p. 155°). It is sparingly soluble in cold water, but readily dissolves in hot water alcohols, or chloroform.

Reactions. Salicylic acid combines the properties of a carboxylic acid and phenol. Its more important reactions are :

(1) When treated with an alkali carbonate, *mono-metallic salt* is formed by the replacement of carboxylic hydrogen,

$$2C_6H_5{<}^{OH}_{COOH} + Na_2CO_3 \rightarrow 2C_6H_5{<}^{OH}_{COONa} + H_2O + CO_2$$

An alkali hydroxide, on the other hand, replaces both the phenolic and the carboxylic hydrogen atoms, yielding a *dimetallic salt* :—

$$C_6H_4{<}^{OH}_{COOH} + 2NaOH \rightarrow C_6H_4{<}^{ONa}_{COONa} + 2H_2O.$$

Disodium salicylate

The di-metallic salts are decomposed by carbon dioxide with formation of mono-metallic salts.

(2) On treatment with an alcoholic and gaseous hydrogen chloride. it forms an *ester*, such as ethyl salicylate, $C_6H_4(OH)\,COOC_2H_5$. The ester reacts with a cold solution of an alkali, yielding a metallic derivative, such as $C_6H_4(ONa).COOC_2H_5$. When heated with an alkyl halide. the metallic derivative yields a *dialkyl derivative* of the type C_6H_4-$(OCH_3)\,COOC_2H_5$.

(3) Acetyl chloride replaces the phenolic hydrogen by an acetyl group.

$$C_6H_4{<}^{OH}_{COOH} + CH_3COCl \rightarrow C_6H_4{<}^{O.CO.CH_3}_{COOH} + HCl,$$

Acetyl-salicylic acid

while phosphorus pentachloride attacks both the phenolic and the carboxylic groups,

$$C_6H_4{<}^{OH}_{COOH} + 2PCl_5 \rightarrow C_6H_4{<}^{Cl}_{COCl} + 2POCl_3 + 2HCl$$

o-Chlorobenzoyl chloride

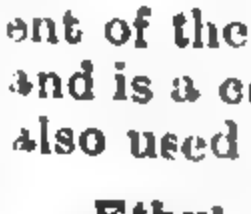
(4) When heated, salicylic acid partly sublimes and partly under-

goes decomposition into phenol and carbon dioxide,

$$C_6H_4(OH).COOH \rightarrow C_6H_5.OH + CO_2$$

the decomposition being complete in the presence of lime.

(5) With ferric chloride, salicylic acid gives a violet coloration (compare phenol).

(6) When salicylic acid is boiled with a solution of calcium chloride and ammonia, it yields a precipitate of basic calcium salicylate,  . The reaction affords a means of separating salicylate acid from its isomerides which do *not* give the corresponding basic salts.

Tests. (1) Add a few drops of ferric chloride ; violet coloration.

(2) Heat with soda-lime ; smell of phenol.

(3) Add a few drops of methyl alcohol and concentrated sulphuric acid, and warm ; characteristic odour of oil of winter green.

Uses. (1) Salicylic acid is a powerful antiseptic and is used in the preservation of foods and such beverages as beer.

(2) Sodium salicylate and acetyl salicylic acid (aspirin) are both employed in medicine.

(3) The methyl, and the β-naphthyl esters also find useful application (*see* below).

12. Salicylic Acid Derivatives.

Methyl salicylate, $C_6H_4<\begin{matrix}OH\\COOCH_3\end{matrix}$, b.p. 224°, is the chief constituent of the oil of wintergreen. It is much used in dental preparations, and is a constituent of synthetic acacia and other flower oils. It is also used as an anti-rheumatic.

Ethyl salicylate, $C_6H_4<\begin{matrix}OH\\COOC_2H_5\end{matrix}$, (b. p. 233°) is similar to the methyl ester, but its odour is finer (resembling that of cardamom).

Phenyl salicylate, $C_6H_4<\begin{matrix}OH\\COOC_6H_5\end{matrix}$, (m. p. 42°) is known as salol and is used as an antiseptic.

β-Naphthyl salicylate, $C_6H_4(OH)COOC_{10}H_7$, is used internally as an antiseptic in intestinal fermentations

Acetylsalicylic acid or aspirin is prepared by heating salicylic acid with acetyl chloride or acetic anhydride (*acetylation*) :

$$C_6H_4<\begin{matrix}O\ H\\COOH\end{matrix} + Cl\,CO.CH_3 \rightarrow C_6H_4<\begin{matrix}O(CO.CH_3)\\COOH\end{matrix} + HCl$$

If forms glistening needles (m. p. 128°), and is used extensively in cases of acute rheumatism, feverish cold and headaches

Sodium salicylate, $C_6H_4<\begin{matrix}COH\\COONa\end{matrix}$, is prepared by neutralizing the acid with sodium *carbonate*. It forms colourless, pearly scales having a sweetish saline taste. It is used in medicine.

QUESTIONS

1. How would you proceed to introduce the —COOH group into the benzene ring ? *(Punjab, B. Sc., 1930)*

2. Describe the different methods available for the synthesis of aromatic acids. In what way do they differ from phenols ? *(Punjab, Inter., 1930)*

3. Describe the laboratory method of preparing a pure speciman of benzoic acid. Give its important properties and tests. *(Punjab, Inter., 1932)*

4. Give a description of the more important derivatives of benzoic acid.

5. How is benzoyl chloride prepared ? To what use is it put in synthetic organic chemistry ? Give one illustrative example.

6. How is benzamide prepared in the laboratory ? Compare its properties with those of acetamide.

7. Describe the usual method of preparing ethyl benzoate. Compare the properties of this ester with ethyl acetate.

8. Describe the preparation of phthalic acid from naphthalene. What happens when the acid is heated ? Give a characteristic test of phthalic acid.

9. How is salicylic acid prepared ? Describe its properties and uses. *(Punjab, Inter., 1944)*

10. Indicate how you would distinguish (*a*) by physical tests and (*b*) by chemical tests, between benzoic acid and salicylic. *(Punjab, B. Sc., 1923)*

11. Write notes on :—
(*a*) Schotten-Baumann reaction; (*b*) Kolbe's reaction.
(*c*) Fluorescein reaction; (*d*) Friedel and Crafts' reaction

12. A monobasic acid gave, on analysis, the undermentioned data. Calculate the empirical formula of the acid, and suggest its structural formula.
0·201 gm. gave 0·308 gm. of CO_2 and 0·045 gm of H_2O. 0·301 gm. gave 0·282 gm of AgBr. 0·402 gm. were neutralized by 20 c. c. of N/10 alkali, [Ag = 108. Br = 80]. *(Punjab, Inter., 1942)*

[*Ans.* $C_7H_5O_2Br$; $C_6H_4 < \begin{matrix} Br \\ COOH. \end{matrix}$]

CHAPTER 36

OXIDIZING, REDUCING AND CATALYTIC AGENTS USED IN ORGANIC CHEMISTRY

1. Oxidizing Agents. The following substances are usually employed as oxidizing agents in organic chemistry :—

(1) *Potassium Permanganate.* This reagent is used both in the acid and the alkaline solution. In the presence of an excess of dilute sulphuric acid, it yields *five* equivalents of available oxygen,

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

while in an alkaline solution it gives only *three* equivalents :—

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O.$$

In the presence of dilute sulphuric acid, it is used to estimate the strength of a solution, containing oxalic acid or an oxalate. In an alkaline solution, it is employed (*i*) in the oxidation of a benzene derivative containing a side chain to a carboxylic acid, and (*ii*) to test for the presence of a double or triple bond in an organic compound.

(2) *Potassium Dichromate.* This reagent is invariably used in the presence of a dilute sulphuric acid :—

$$K_2Cr_2O_7 + 4H_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

It is employed for the oxidation of ethyl alcohol to acetaldehyde and to acetic acid. It is also used for the conversion of aniline into aniline black.

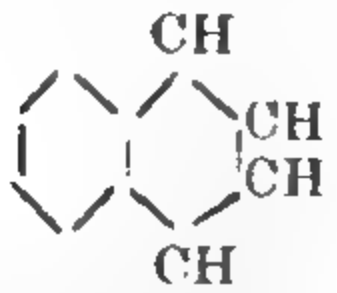
(3) *Lead Chromate.* In the quantitative estimation of carbon and hydrogen in an organic substance containing a halogen, lumps of fused lead chromate are used instead of cupric oxide. This salt, like cupric oxide, acts as a powerful oxidizing agent at high temperatures :—

$$2PbCrO_4 \rightarrow 2PbO + Cr_2O_3 + 3O$$

Lead chromate is preferred to cupric oxide because lead halides, that are here produced, are less volatile and more stable than the corresponding copper compounds.

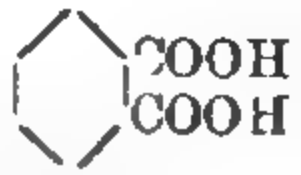
(4) *Nitric Acid.* This reagent finds a wide application as an oxidizer of organic substances. An important example of the complete oxidation of a substance by *fuming* nitric acid is the Carius method for the estimation of halogens, sulphur and phosphorus. When *concentrated* nitric acid is added to cane sugar, copious brown fumes of nitrogen dioxide are evolved, and the sugar is oxidized to oxalic acid. Toluene and other derivatives of benzene containing a side-chain, when boiled with *dilute* nitric acid, give aromatic acids.

(5) *Sulphuric Acid.* An important example of the use of concentrated sulphuric acid as an oxidizing agent is the Kjeldahl method for the estimation of nitrogen in an organic compound. The substance is heated with concentrated H_2SO_4 and $KHSO_4$, whereby the carbon present in the compound is oxidized to CO_2, while nitrogen is left as ammonium sulphate. Fuming sulphuric acid is commercially employed for the oxidation of naphthalene to phthalic acid, under the catalytic influence of mercuric sulphate or metallic mercury :—



Naphthalene

$$+ \ 9O \rightarrow$$



Phthalic acid

$$+ \ 2CO_2 + H_2O$$

(6) *Manganese Dioxide*, in the presence of sulphuric acid is employed for the oxidation of the side-chain of a benzene homologue to an aldehyde group :—

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + O$$

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + 2O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5.CHO} + H_2O$$

(7) *Hydrogen Peroxide.* Hydrogen peroxide in the presence of a ferrous salt (**Fenton's reagent**) is used for oxidizing the hydroxy acids ; *e.g.*,

$$\underset{\text{Lactic acid}}{CH_3.CH(OH).COOH} + H_2O_2 \rightarrow \underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + 2H_2O$$

(8) *Sodium Hypobromite.* This reagent is used in the estimation of urea :—

$$NH_2.CO.NH_2 + 3NaOBr \rightarrow CO_2 + N_2 + 2H_2O + 3NaBr$$

The evolved nitrogen is measured over a strong solution of potassium hydroxide, which absorbs carbon dioxide.

(9) *Cupric Oxide.* This substance is used as an oxidizing agent in organic analysis for the detection and estimation of carbon and hydrogen. *Fehling's solution* which is an alkaline solution of cupric oxide in the presence of Rochelle salt, is used for the detection and estimation of aldehydes and sugars.

(10) *Air.* Atmospheric oxygen is used for oxidizing organic substances in the presence of finely-divided platinum, or enzymes called *oxydases.* Thus, methyl alcohol vapour, when mixed with air and passed over platinum black, gives formaldehyde :

$$2CH_3OH + O_2 \rightarrow 2H.CHO + 2H_2O.$$

A dilute solution of ethyl alcohol in the form of weak wines is oxidized to acetic acid under the catalytic effect of *mycoderma aceti.*

2 Reducing Agents. The following are the methods of reduction generally employed in Organic Chemistry :—

(1) **Reduction with Nascent Hydrogen in Acid Solution.** The most important agent used in the reduction of organic substances is nascent hydrogen, *i.e.*, hydrogen generated in the presence of the substance to be reduced. Reduction with nascent hydrogen is effected in an acid, alkaline, or a neutral solution. As examples of reduction by means of nascent hydrogen in acid solution we have :—

(*i*) *Tin and Hydrochloric Acid.* This mixture is used in the laboratory for the reduction of aromatic nitro-compounds to the amino-compounds, the metal being converted into stannous, and then into stannic chloride :

$$Sn + 2HCl \rightarrow SnCl_2 + 2H$$

$$SnCl_2 + 2HCl \rightarrow SnCl_4 + 2H$$

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \rightarrow \underset{\text{Aniline}}{C_6H_5.NH_2} + 2H_2O$$

(*ii*) *Stannous Chloride and Hydrochloric Acid.* These sometimes give better yields than tin and hydrochloric acid. The reduction of

benzene diazonium chloride to phenylhydrazine may be mentioned as an example of this method.

$$C_6H_5N_2Cl + 4H \rightarrow C_6H_5NH.NH_2.HCl$$

(*iii*) *Iron and water in the presence of a little* hydrochloric acid is employed for the commercial preparation of aniline from nitrobenzene.

(*iv*) *Hydriodic Acid.* The reducing action of this reagent is due to its tendency to yield nascent hydrogen at moderate temperatures :—

$$2HI \rightleftharpoons 2H + I_2$$

The main use of this reagent is to reduce the hydroxyl group present in an organic compound to a hydrogen atom. Thus, glycerol, on being heated with hydrogen iodide at 275° in a sealed tube, yields propane :—

$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} + 6HI \rightarrow \underset{\text{Propane}}{CH_3.CH_2\,CH_3} + 3H_2O + 3I_2$$

Similarly, hydroxy acids are corresponding carboxylic acids. Thus, tartaric acid, on being heated with concentrated hydriodic acid in the presence of red phosphorus, yields succinic acid :—

$$\underset{\text{Tartaric acid}}{\begin{matrix}CH(OH)COOH\\|\\CH(OH)COOH\end{matrix}} + 4HI \rightarrow \underset{\text{Succinic acid}}{\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}} + 2H_2O + 2I_2$$

The red phosphorus serves to keep the concentration of hydriodic acid practically unchanged throughout the reaction, as it attacks the iodine produced, reconverting it, in the presence of water, into hydriodic acid.

(2) Reduction with Nascent Hydrogen in Alkaline Solution. The various methods employed for effecting reduction in alkaline solution are :

(*i*) *Metallic Sodium and Absolute Alcohol.* This mixture is employed for the reduction of alkyl cyanides to primary amines :—

$$C_2H_5OH + Na \rightarrow C_2H_5ONa + H$$
$$RC \equiv N + 4H \rightarrow R\,CH_2.NH_2$$

Sodium and boiling amyl alcohol reduce benzoic acid to hexahydrobenzoic acid :

$$C_6H_5COOH + 6H \rightarrow C_6H_{11}\,COOH$$

(*ii*) *Sodium Amalgam and Water.* This mixture is employed mainly for reducing olefine derivatives to the corresponding saturated compounds ; *e.g.*,

$$Na + H.OH \rightarrow NaOH + H$$
$$\underset{\text{Cinnamic acid}}{C_6H_5CH=CH\,COOH} + 2H \rightarrow \underset{\beta\text{-Phenylpropionic acid}}{C_6H_5.CH_2.CH_2COOH}$$

The alkali produced in the reaction sometimes exerts a destructive action on the products of reduction. *Aschan's method* to overcome this difficulty consists in passing a current of CO_2 through the reaction mixture, and thus converting the sodium hydroxide into the bicarbonate as fast as produced

(*iii*) *Zinc-dust and Sodium Hydroxide.* An example of the use of this reagent is the conversian of *o*-nitraniline into *o*-phenylenediamine :—

$$Zn + 2NaOH \rightarrow Zn(ONa)_2 + 2H$$

o-Nitraniline — *o*-Phenylene diamine

(3) **Reduction with Nascent Hydrogen in Neutral Solution.** A number of reductions occur most readily in the absence of free acid or alkali, and may be brought about by the following reagents :

(*i*) *Zinc-Copper Couple and Alcohol.* This reagent is used for reducing alkyl halides to paraffin hydrocarbons ; *e g.*,

$$C_2H_5I + 2H \rightarrow C_2H_6 + HI.$$

(*ii*) *Zinc-dust and Water.* This is found most suitable for reducing aromatic nitro-compounds to the corresponding hydroxylamines : *e.g.*,

$$Zn + 2H.OH \rightarrow Zn(OH)_2 + 2H$$

$$\underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + 4H \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NH.OH} + H_2O.$$

(*iii*) *Aluminium Amalgam and Water.* This is a useful reducing agent for converting ketones into secondary alcohols,

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2H \rightarrow \underset{\text{Isopropyl alcohol}}{CH_3.CH(OH).CH_3},$$

and also for reducing nitro-derivatives to hydroxylamines.

(4) **Electrolytic Reduction.** This is an important method of effecting reduction with nascent hydrogen in an electrolytic cell. The most important example of the use of this method is the reduction of nitrobenzene. The products formed depend upon : (a) nature of the solution (*i.e.*, whether acidic, alkaline or neutral), and its concentration, (*b*) temperature, (*c*) strength of the current used, and (*d*) the materials of which the electrodes are made. By varying these conditions, nitrobenzene may be reduced to give a number of products, namely, *p*-amino phenol, azoxybenzene, azobenzene, hydrazobenzene and aniline.

(5) **Catalytic Reduction with Hydrogen (Hydrogenation).** A very important method of converting the unsaturated into the saturated compounds and of reducing the aromatic compounds to hexamethylene derivatives consists in passing the vapour of these compounds over heated metals, in a very finely-divided condition. The method was thoroughly investigated by **Sabatier** and **Senderens.** Of the various metals used, finely-divided nickel was found to give the best results. The method has acquired considerable commercial importance, and is nowadays used for the manufacture of **artificial ghee** by the hydrogenation of oils. The process consists in passing hydrogen through the heated oil having finely-divided nickel suspended in it. The unsaturated liquid glycerides are thereby converted into the corresponding saturated compounds, which are solid fats.

$$\underset{\text{Olein}}{C_3H_5(O.COC_{17}H_{33})_3} + 6H \rightarrow \underset{\text{Stearin}}{C_3H_5(C.CO.C_{17}H_{35})_3}$$

(6) **Other Methods of Reduction.** The following examples illustrate the use of other reducing agents in organic chemistry :

(*i*) Reduction of solid diazonium salts to hydrocarbons by means of *alcohol* :—

$$C_6H_5N_2Cl + CH_3CH_2OH \rightarrow C_6H_6 + N_2 + HCl + CH_3.CHO$$

(*ii*) Reduction by means of *ammonium sulphide* in alcoholic solution is especially useful for the partial reduction of polynitro compounds.

3. Catalytic Agents. Catalytic agents play a far greater part

in organic chemistry than they do in the inorganic. The following are some examples of reactions that are catalysed by the presence of suitable agents :—

(1) *Oxidation.* Most of the primary and the secondary alcohols readily lose hydrogen when heated in contact with a catalyst. Thus. ethyl alcohol gives an 80 per cent yield of acetaldehyde when passed over zinc heated at 660°.

$$CH_3.CH_2OH \rightleftharpoons CH_3.CHO + H_2$$

Isopropyl alcohol gives an almost quantitative yield of acetone, when its vapour is passed over reduced copper heated at 250° to 320°C.

The oxidation of methyl alcohol to formaldehyde by air in the presence of finely-divided platinum, and that of dilute alcoholic liquors to acetic acid by the ferment *mycoderma aceti* are other familiar examples. An oxidation reaction of great commercial importance is the conversion of naphthalene into phthalic acid by fuming sulphuric acid in the presence of metallic mercury or mercuric sulphate.

(2) *Reduction.* (*See* Catalytic Reduction, *p.* 298.)

(3) *Chlorination and Bromination.* These reactions are catalysed by finely-divided iron, aluminium, or iodine, and also by sunlight.

(4) *Hydrolysis.* Hydrolysis of esters and of sugars by dilute acids and enzymes are catalytic reactions.

(5) *Dehydration.* Alumina heated at 400° brings about the dehydration of alcohols and amides. *e.g.*,

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$
$$CH_3CONH_2 \rightarrow CH_3CN + H_2O.$$

(6) *Friedel and Crafts' Reaction.* This is employed for preparing homologues of benzene and several other classes of aromatic compounds. and is based on the use of anhydrous aluminium chloride as the catalyst

(7) Combination af *acetylene* with the elements of water to give acetaldehyde,

$$CH{\equiv}CH + H_2O \rightarrow CH_3.CHO.$$

is a commercially important reaction, which is carried out in the presence of mercuric sulphate,

(8) Conversion of *acetaldehyde* into aldol, ethyl acetate, and paraldehyde (p. 121, Sec 9).

The above are but a few of a countless number of catalytic reaction taking place in the realm of organic chemistry. The assimilation of carbon dioxide by plants in the presence of chlorophyll and sunlight the assimilation of food by animals, the process of respiration, and numerous other anabolic changes taking place in plants and animals are practically all catalytic in nature.

"People hate love. Is it? But they reason is This that may dornot take love as it is. Let us, Students! unites us make them know what it means with a sincere mind & burning desire." Hi Raghvendra Gaur Kents.

QUESTIONS

1. Name the substances usually employed as oxidizing agents in organ chemistry. Explain your answer by taking specific examples. (*Punjab, Inter.*, 192

2. What methods of reduction are employed in Organic Chemistry ? Expla your answer by taking specific examples. (*Punjab, Inter.*, 19

3. Write a note on "The Use of Catalytic Agents in Organic Chemistry (*Punjab, Inter.*, 19

APPENDIX I

ATOMIC NUMBERS AND ATOMIC WEIGHTS OF SOME ELEMENTS

Element	Symbol	Atomic No.	Approximate Atomic Weight
Bromine	Br	35	80
Calcium	Ca	20	40
Carbon	C	6	12
Chlorine	Cl	17	35·5
Hydrogen	H	1	1
Iodine	I	53	127
Nitrogen	N	7	14
Oxygen	O	8	16
Phosphorus	P	15	31
Platinum	Pt	78	195
Potassium	K	19	39
Silver	Ag	47	108
Sodium	Na	11	23
Sulphur	S	16	32

APPENDIX II

TENSION OF WATER VAPOUR IN MILLIMETRES OF MERCURY

Temp. °C	Vapour pressure	Temp. °C	Vapour pressure	Temp. °C	Vapour pressure
5	6·5	17	14·4	29	29·8
6	7·0	18	15·4	30	31·5
7	7·5	19	16·3	31	33·4
8	8·0	20	17·4	32	35·4
9	8·6	21	18·5	33	37·4
10	9·2	22	19·7	34	39·5
11	9·8	23	20·9	35	41·8
12	10·5	24	22 2	36	44·2
13	11·2	25	23·5	37	46·7
14	11 9	26	25·0	38	49·3
15	12·7	27	26·5	39	52·0
16	13·5	28	28·1	40	54·9

APPENDIX III

USEFUL MEMORANDA

Weight of 1 c.c. of hydrogen at N.T.P.=0·00009 gm.
One litre=61 cubic inches=0·22 gallon=1 8 pint=35·2 fluid oz.
1 fluid oz =28·4 c c.
1 gram =15·4 grains.
1 lb. =453·6 grams. 1 oz.=28·35 gm.
1 Kilogramme=2·2 lb.

INDEX

Subject	Chap.	Sec.
Abel's apparatus	7	16
Absolute alcohol	10	8
Acetals	12	5
Acetamide	14	7
Acetanilide	30	5
Acetates	13	13
Acetic acid	13	[illegible]
Acetic anhydride	14	5
Acetaldehyde	12	11
,, ammonia	12	5
,, resin	12	5
Acetone	12	15
,, dicarboxylic acid	20	10
Acetophenone	34	7
Acetyl chloride	14	2
Acetylene	8	7
,, homologues of	8	8
Acetylsalicylic acid	35	11
Acid amides	14	6
,, anhydrides	14	4
,, chlorides	14	1
,, nitriles	14	8
Acids, monocarboxylic	13	1
,, polybasic	20	1
Aconitic acid	20	10
Acrolein	19	3
Acyl groups	13	1
Addition compounds	8	2
,, reactions	8	2
,, ,, mechanism of	8	3
Air condenser	2	4
Alcoholic beverages	10	16
,, fermentation	10	10
Alcohol, absolute	10	8
,, denatured	10	7
Alcohol industry, by-products of	10	9
Alcoholometry	10	12
Alcohols, aliphatic	10	1
,, distinction between primary, secondary and tertiary.	[illegible]	5
Alcohols, polyhydric	19	1
Aldehyde resins	12	5
Aldehydes, aliphatic	12	1
,, aromatic	34	3
,, reactions in which they differ from ketones	12	5
Aldol	12	11
,, condensation	12	11
Aliphatic compounds	6	2
Alkyl benzenes	27	1
,, cyanides	14	8
,, groups	7	12
,, halides	9	1
,, nitrites	17	9
Amines, aliphatic	17	1
,, distinction between primary, secondary and tertiary	17	6
Amino-acetic acid	30	10
Amino-acids	18	7
Aminoazo-compounds	18	6
Aminoazo-compounds aromatic	31	4
Amygdalin	30	1
Amyl acetate	34	4
Amylase	15	[illegible]
Aniline	22	8
Animal charcoal, treatment with	30	3
Anodic oxidation	2	11
Antifebrin	7	3
Argol	30	5
,,	10	9
Aromatic acids	20	8
,, compounds	35	1
,, alcohols	6	2
,, aldehydes	34	1
,, ketones	34	3
Artificial *ghee*	34	6
,, ,,	8	2
Ascent and descent of	16	3
Aspirin	17	7
Asymmetric carbon atom	35	11
Atomic number	21	6
Azo-dyes	6	8
Baeyer's reagent	31	4
Bacillus, macerans	8	2
Bacterium aceti	12	15
Bakelite	13	8
,,	12	9
Barley sugar	33	7
Beer	22	7
Beilstein's test	10	16
Benzal chloride	3	6
Benzadehyde	28	10
Benzamide	34	4
Benzene	35	6
,, diazonium sulphate	25	1
,, homologues of	31	2
,, isolation of	27	1
,, properties of	24	4
,, structure of	25	5
,, sulphonic acid	25	8
,, ,, chloride	32	4
Benzine	32	5
Benzoic acid	7	14
,, anhydride	35	3
Benzoin condensation	35	5
Benzophenone	34	4
Benzotrichloride	34	8
Benzoyl chloride	28	10
Benzoylation	35	4
Benzyl alcohol	35	4
Benzylidene chloride	34	2
Benzylamine	28	10
Benzyl chloride	30	7
Bisulphite compounds	28	9
Biuret	28	4
,, reaction	12	3
Blue-print papers	23	3
Boiling-point determination	23	11
Bomb-furnace	20	17
Brandy	2	6
Bromamide reaction	4	16
	10	3
	14	

Subject	Chap.	Sec.
Bromobenzene	28	7
Bruhl's apparatus	2	3
Buchner funnel	2	2
Butanes	7	10
Butyl alcohols	10	2
Butyric acid	13	15
Cane sugar	22	7
Cannizzaro's reaction	12	8
" "	34	4
Caramel	22	7
Carbinol	10	2
Carbohydrates	22	1
Carbolic acid	33	7
Carbon, detection of	3	2
" estimation of	4	2
Carbon atom, tetravalency of	6	2
Carbonic acid, derivatives of	23	1
Carbon tetrachloride	9	15
Carbon valencies, equivalence of	6	2
Carbonyl chloride	23	2
Carbonyl group	12	1
Carboxyl group	13	1
" " detection of	13	4
" " reactions of	13	3
" " structure of	13	5
Carbylamine reaction	9	13
" "	17	6
" "	30	3
Carius method	4	5
" "	4	6
Catalytic agents	39	3
Cellulose	22	9
Centrifugal machine	2	2
Champoigne	10	16
Chloral	12	13
" hydrate	12	14
Chloro-acetic acid	18	2
Chlorobenzene	28	6
Chloroform	9	13
Chlorohydrin	8	2
Cider	10	16
Citric acid	20	10
Claisen's distilling flask	2	7
" reaction	34	4
Coal, dry distillation of	24	2
Coal tar industry	24	1
" " fractional distillation of	24	3
Coffey still	10	7
Combustion	4	2
Condensation	12	16
" external	12	16
" internal	12	16
Co-ordinate link	6	12
Counter-current principle	22	7
Coupling	31	4
Co-valency	6	11
Cracked gasoline	7	15
Cracking	7	15
Cream of tartar	20	9
Crotonal dehyde	12	17
Crotonic acid	12	17
" aldehyde	12	17
Crum *Brown and Gibbon's* rule	26	3
Crystallization	2	2

Subject	Chap.	Sec.
Cuprour acetylide	8	7
Cyanhydrins	12	4
Defecation	22	7
Denatured alcohol	10	7
Desiccating agents	2	12
Destructive distillation of coal	24	2
Dextrose	22	2
Diastase	10	7
"	22	8
Diazo-reaction	31	1
Diazonium salts	31	1
Diazotization	31	1
Dichloroethane	9	11
Dichloromethane	9	10
Diethyl-ether	11	3
Diffussion process	22	7
Dimethyl-aniline	30	9
Dimethyl-ether	10	6
Dimethyl psendo-nitrol	10	19
m-Dinitrobenzene	29	8
Directive influence of substituents	26	3
Disaccharides	22	1
Distillation	2	4
" fractional	2	5
" under reduced pressure	2	7
Distilled liquors	10	16
Double bond	8	3
Drying of organic substance	2	12
Drying oils	16	2
Dumas' method	4	8
Electrons	6	8
Electrovalency	6	11
Empirical formula ; calculation of	5	1
Enzymes	10	10
Equivalent weight, determination of	5	8
Ester, identification of	15	6
Esterification	15	1
Esters	15	1
Esters and salts, distinction between	15	7
Etard's reaction	34	4
Ethanal	12	11
Ethane	7	3
" acid	13	8
" diacid	20	2
" saturated nature of	7	4
Ethenoid linkage	8	3
Ether, diethyl	11	3
Ethers	11	1
Ethyl acetate	15	2
Ethyl alcohol	10	7
" " distinction from methyl alcohol	10	8
Ethyl alcohol, estimation of	10	15
" " structure of	6	6
" " uses of	10	17
Ethyl benzoate	35	7
" bromide	9	7
" butyrate	15	5
" chloride	9	6

Subject	Chap.	Sec.
Ethyl cinnamate	15	5
,, hydrogen sulphate	10	12
,, ,, ,,	15	3
,, iodide	9	8
,, isovalerate	15	5
Ethyl malonate	15	5
,, nitrite	15	4
,, salicylate	35	11
Ethylamine	17	4
Ethylammonium hydroxide	17	4
Ethylene	8	2
,, constitution of	8	3
,, linkage	8	3
,, separation from a mixture	8	2
Ethylene chloride	9	11
,, glycol	19	2
Ethylidene chloride	8	3
,, ,,	9	11
External compensation	21	6
Extraction with solvents	2	10
Fats and oils	16	1
Fatty acids	13	1
Fehling solution	20	8
Fermentation, theory of	10	11
Fermentation and enzyme action	10	10
,, ,, ,, ,,	10	11
Ferments	10	10
Filter pump	2	2
Filtering flask	2	2
Fittig's synthesis	9	4
,, ,,	27	2
Flash point	7	16
Fluorescein reaction	35	8
Formaldehyde	12	7
,, constitution of	12	10
,, uses of	12	11
Formalin	12	9
Formic acid	13	6
Fortified wines	10	16
Fractional distillation	2	5
Fractionating columns	2	5
Friedel and Crafts' reaction	25	5
,, ,, ,, ,,	27	2
,, ,, ,, ,,	34	4
Fructose	22	3
Fruit sugar	22	3
Fuel oil	7	15
Fusel oil	10	7
,, ,,	10	9
Galalith	12	9
Gas oil	7	15
Gaseous hydrocarbons, of determination of formulae of	5	8
Gasoline	7	15
Gattermann's reaction	31	4
General formula	7	6
Gin	15	16
Glacial acetic acid	13	10
Glucosazone	22	3
Glucose	22	2
,, conversion into fructose	22	5
,, syrup	22	2

Subject	Chap.	Sec.
Glucose and fructose, distinction between	22	4
Glucosides	22	6
Glycerine	19	3
Glycerol	19	3
Glyceryl monoformate	13	6
Glyceryl trinitrate	19	3
Glycine	18	7
Glycol	19	2
Glycollic acid	18	4
Glycols	19	2
Gram-molecular volume	5	3
Grape sugar	22	2
Green oil	24	3
Grignard reagents	9	4
,, ,,	28	4
Grove's process	9	2
Halogen derivatives, aliphatic	9	1
,, ,, aromatic	28	1
Halogens, detection of	3	6
,, estimation of	4	5
Heavy oil	24	3
Heavy oil and paraffin	7	15
Hexamine	12	8
Hinsberg's method	17	5
Hofmann's bromamide reaction	14	7
Homologues series	7	6
Hot water funnel	2	2
Hufner's method	23	3
Hydrogen, detection of	3	2
,, estimation of	4	2
Hydrogenation	8	4
,, of oils	10	3
Hydrolysis	9	4
Hydroxyacetic acid	18	4
Hydroxy acids	18	3
Hydroxyazo compounds	31	8
Hypnone	34	7
Indophenine reaction	26	3
Internal compensation	21	6
Inversion	22	7
Invert sugar	22	7
Invertase	10	10
Iodobenzene	28	8
Iodoform	9	14
Isobutane	7	9
,,	7	10
Isomeric change	6	4
Isomerides	6	1
Isomerism	6	1
,,	7	9
,, of benzene derivatives	26	1
Isomerization	6	4
Isomers	6	1
Isonitroparaffins	17	9
Isopropyl acetate	10	19
,, alcohol	10	10
,, chloride	7	8
Kerosene oil	7	15
Ketones	12	3
,,	12	15
,, (aromatic)	34	6
Kjeldahl's method	4	4

Subject	Chap.	Sec.
Kolbe's reaction	7	3
" "	7	7
" "	33	7
Korner's absolute method	26	2
Lactic acid	18	5
Lactic acids, optical isomerism of	21	7
Lactic acid fermentation	10	10
Lassaigne's test	3	4
" "	3	6
Lead acetate	13	13
Le Bel and *van't Hoff's* theory	21	5
Levulose	22	3
Liebermann's nitroso reaction	17	6
Light oil	24	3
Lubricating oils	7	15
Malonic acid	20	5
Malt	10	7
" extract	10	7
Maltase	10	7
Mannitol	22	3
Markownikoff's rule	7	7
Marsh gas	7	1
Mashing	10	7
Melting-point determination	2	13
Mesityl oxide	12	15
Mesitylene	27	6
Meso-tartaric acid	21	4
Metaldehyde	12	11
Metamerism	6	5
Methanal	12	7
Methane	7	1
" acid	13	6
" saturated nature of	7	2
Methane, the parent hydrocarbon of the aliphatic series	8	10
Methane and ethane, structural relation of	7	5
Methylated spirit	10	7
Methyl acetate	15	5
" alcohol	10	5
" alcohol, structure of	6	6
" chloride	9	5
" group	7	5
" hydrogen sulphate	10	6
" iodide	9	5
" amine	17	3
" aniline	30	8
" methane	7	5
" ammonium hydroxide	17	3
Methylene chloride	9	10
Middle oil	24	3
Mineral oils	16	7
Molecular formula, determination of	5	2
Molecular structure	6	2
Molecular weights of volatile substances	5	3
Molecular weights of non-volatile substances	5	5
Molecular weights, freezing point method	5	6
Molecular weights, boiling point method	5	7
Monochloropropanes	7	8
Monohydric alcohols	10	1
Monosaccharides	22	1
Motor fuel	10	17
Naphtha	7	15
Naphthyl salicylate	35	11
Natural gas	7	14
Neutrous	6	8
m-Nitraniline	30	6
Nitration	29	1
Nitro compounds, aromatic	29	1
" identification of	29	6
" reduction of	29	4
Nitrobenzene	29	7
Nitrogen, detection of	3	4
" estimation of	4	4
Nitroglycerine	19	3
Nitrolic acids	10	5
Nitrometer	4	4
Nitro-paraffins	17	9
" distinction from alkyl nitrites	17	10
Nitros-amines	17	6
p-Nitroso-dimethyl-aniline	30	9
Non-drying oils	16	2
Nuclear charge	6	9
Nucleus	6	8
Oil of bitter almonds	34	4
Oil of mirbane	29	7
Oil-gas	7	15
Olefines	8	4
Oleic acid	13	17
" "	16	1
Olein	16	1
Optical activity	21	2
" " and polarimetry	21	1
Organic acids, determination of formulæ of	5	8
Organic bases, determination of formulæ of	5	8
Organic chemistry, definition of	1	1
" " importance of	1	3
" " scope of	1	1
" compounds elements present in	1	3
Organic and inorganic chemistry, reasons for distinction between	1	2
Organic substances, drying of	2	12
" " purification of	2	1
" " sources of	1	4
" " systamatic investigation of	6	7
Orientation of benzene derivatives	26	2
Osazones	22	2
Oxalic acid	20	2
" " salts of	20	3
Oxidizing agents	36	1
Oximes	12	4
Oxygen, detection of	3	3
" estimation of	4	3
Ozokerite	7	14
Ozonides	8	2

Subject	Chap.	Sec.
Plaimitic acid	13	16
Palimitic acid	16	1
Palmitin	16	1
Paracetaldehyde	12	11
Paraffin wax	7	15
Paraffins	7	7
,, natural sources of	7	14
Paraformaldehyde	12	[illegible]
Patart Process	10	6
Pauli's principle	6	8
Pentanes	7	11
Perkin's reaction	34	4
Petrohol	10	19
Petrol	7	15
Petroleum, industry	7	15
,, coke	7	15
,, ether	7	15
Phenolic acids	35	9
Phenol	33	7
,, isolation of	24	5
Phenols	33	1
Phenyl chloride	28	6
Phenyl salicylate	35	11
m-Phenylene diamine	29	8
Phenyl hydrazine	31	7
Phenyl hydrazones	12	4
Phorone	12	15
Phosgene	23	2
Phosphorus, detection of	3	7
,, estimation of	4	6
Phthalic acid	35	8
,, anhydride	35	8
Phthalimide	35	8
Picric acid	33	8
Pitch	24	3
Plane of polarization	21	1
Polar compound	6	11
Polarimeter	21	3
Polarisation of light	21	1
Polybasic acids	20	[illegible]
Polyhydric alcohols	19	1
Polymerization	12	16
Polysaccharides	22	[illegible]
Port	10	16
Primary, secondary and tertiary alcohols	10	[illegible]
distinction between	10	5
Propane	7	8
Propane-triol	19	3
Propanone	12	15
Propyl alcohol	10	18
,, chloride	7	8
Protons	6	8
Pseudo acids	17	9
,, ,, nitrols	10	5
Purity, methods of testing	2	13
Pyroligneous acid	10	6
Qualitative elementry analysis	3	1
Quantitative elementry analysis	4	1
Quaternary ammonium compounds	17	8
,, structure of	17	8
Quick, vinegar process	13	9
Racemic acid	21	4
Raw spirit	10	7
Reducing agents	36	2
Reflux condenser	2	2
Relative method of orientation	26	2
Rimini's test	12	[illegible]
Rochelle salt	20	8
Rongalite	12	9
Rosenmund's reaction	12	7
Rum	10	16
Sabatier and Senderens' reaction	7	7
Salicylaldehyde	34	5
Salicylic acid	35	10
Salol	35	11
Sandmeyer's reaction	28	2
Saponification	15	[illegible]
,, of fats and oils	16	4
Sarcolactic acid	21	7
Saturated compound, definition of	7	2
,, compounds	6	2
,, hydrocarbons	7	1
Schiff's reaction	12	[illegible]
Semi-drying oils	16	2
Separating funnel	2	[illegible]
Scho'ten-Baumann reaction	35	[illegible]
Shale	7	15
Sherry	10	16
Silver acetylide	[illegible]	7
,, mirror test	12	[illegible]
Siwolowoff's method	2	13
Soap	16	4
Soaps	16	5
Soda-lime test	[illegible]	4
Sodium acetate	13	13
,, oxalate	20	3
,, salicylate	35	11
Sorbitol	22	2
Soxhlet extractor	2	10
Spent wash	10	9
Spirit, methylated	10	7
Starch	22	[illegible]
Steam distillation	2	8
,, ,, principle of	2	8
Stearic acid	13	16
Stearin	16	1
Stereochemistry	21	5
Strain theory	8	3
Structural formula, determination of	6	6
Structure	6	2
Substitution	6	3
,,	7	2
,, products	7	2
,, ,,	8	2
Succinic acid	20	6
Sucrose	22	7
Sugar of lead	13	13
Sugars	22	1
Sulphitation	22	7
Sulphonic acids, aromatic	32	1
Sulphur, detection of	3	5
,, estimation of	4	6
Tar	7	1
Tartar	10	9
,, emetic	20	9

Subject	Chap.	Sec.
Tartaric acid	20	8
Tartaric acid constitution of	20	8
,, ,, stereoisomerism of	21	4
Thiophene	25	3
,,	37	3
Toluene	27	5
,, isolation of	24	4
Toluidines	30	8
Triple bond	8	7
Unsaturated compounds	6	2
,, hydrocarbons	8	1
Unsaturation, tests for	8	2
Urea	23	3
,, nitrate	23	3
,, oxalate	23	3
Ureameter	23	3
Urease	23	3
Urotropine	12	9
Vacuum desiccator	2	12
Valency electrons	6	10
Vaseline	7	15
Verdigris	13	13
Victor Meyer's method for molecular weight determination	5	4
Victor Meyer's method for distinguishing between primary, secondary and tertiary alcohols	10	5
Vinegar	13	9
Vital force theory	1	1
Waxes	15	8
Westron	8	7
Whisky	10	16
Williamson's synthesis	11	2
Wine	10	16
Wood, destructive distillation of	10	6
Wood gas	10	6
,, spirit	10	6
,, tar	10	6
Wurtz' reaction	7	3
,, ,,	7	7
,, ,,	9	4
Xylenes	27	6
Yeast	10	11
Zymase	10	7
,,	10	10

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
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14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9 3 6 9	12 15 19 12 14 17	22 25 28 20 23 26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 9 3 6 8	11 14 17 11 14 17	20 23 26 19 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 6 8 3 5 8	11 14 16 10 13 16	19 22 24 18 21 23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3 5 8 3 5 8	10 13 15 10 12 15	18 20 23 17 20 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7 2 4 7	9 12 14 9 11 14	17 19 21 16 18 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7 2 4 6	9 11 13 8 11 13	16 18 20 15 17 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 [illegible] 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
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398